

DEVELOPMENT OF A LONG LIFE THERMAL CELL

by

H. J. Goldsmith and J. R. Moser

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6101 FALLS ROAD

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TECHNICAL MANAGEMENT
NASA LEWIS RESEARCH CENTER
CLEVELAND, OHIO
SPACE POWER SYSTEMS
M. R. UNGER

1 CATALYST RESEARCH CORPORATION,
6101 FALLS ROAD
BALTIMORE, MARYLAND 21209

ABSTRACT

The objective of this program is the development of a reliable thermal cell operating at 800°F for 48 to 144 hours depending on current drain, ranging from 87.5 ma to 264 ma. The cell is to contain a magnesium anode, copper oxide cathode, separator, and eutectic chloride electrolyte.

The main emphasis of the work reported on herein was on the development of a reliable cathode (14 A hr capacity) and separator. Five cathode configurations and five CuO/Cu₂O chemical compositions were designed and evaluated. Tests resulted in the choice of a copper needle configuration while 100% CuO and 100% Cu₂O gave comparable discharge characteristics.

Efficiencies between 80 to 90 percent have been achieved and Vitron E was established as the best separator of the five tested. The report contains conclusions and results of the following tests: potential vs. current, potential vs. time, stability, surface area, porosity and solubility of the cathode; stability of the anode; separator resistance and stability; thermal oxidation of copper to CuO and Cu₂O; and soundness of the cell under various dynamic conditions.

Work is continuing using full, sealed cells containing 100% CuO and 100% Cu₂O needle cathodes with vitron separator. Compatibility of the various cell construction materials is being closely studied.

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DEVELOPMENT OF A LONG LIFE THERMAL CELL

CONTRACT OBJECTIVES

The research under contract NAS 3-8517 is directed toward the development of a thermal battery using a magnesium anode, copper oxide cathode, a separator and eutectic fused salt, 59 mole percent lithium chloride plus 41 mole percent potassium chloride, operating at 800°F (427°C). A development is aimed to achieve a life of 48 hours or 144 hours depending upon the current drain from the cell. The work is being carried out for the National Aeronautics and Space Administration, with Mr. J. E. Dilley as the contracting officer, Mr. M. Unger and Dr. L. Thaller as technical monitors. The principal investigator is James R. Moser.

GENERAL INTRODUCTION

The overall cell that is to emerge from this study is Mg/LiCl-KCl//LiCl-KCl/Cu₂O-CuO. The principal point of investigation concerns the technology involved in preparing suitable cathodes. Chemically, this requires a method by which pure copper can be preferentially oxidized to either cupric oxide or cuprous oxide or a mixture of both. Experimentation has shown that heating of pure copper in air at 900° to 1,000°C will produce essentially 100% pure cupric oxide. By placing cupric oxide in a nitrogen or argon atmosphere at 900 to 1,000°C, a portion of the cupric oxide can be reverted to cuprous oxide. With extended heating in an inert gas, an electrode can be made that is essentially pure cuprous oxide.

The sturdiness of the electrode also must be considered when preparing copper oxide cathodes. When initial current is passed, the copper oxide reduces to elemental copper. If the cathode has a very low porosity, it will be encased in a copper sheet causing heavy polarization. This is due to the lack of active material in contact with electrolyte that can be reduced. This might be considered as an extreme case of concentration polarization.

Whenever one works with a powdery substance, such as copper oxide, it can be expected that small particles will be suspended in the electrolyte. Secondly, one would expect some dissolution and chemical reaction in and with a fused chloride electrolyte.

Upon contact of the copper species with an anode, a local oxidation/reduction reaction would occur. The result is a copper clad magnesium anode with a potential much lower than that expected from magnesium. All this implies the use of a separator.

Five different separators were examined for chemical and physical stability in the salt at 427°C. Effect of increased resistance due to the incorporation of a separator in the cell was also examined.

The final proof of these components rests in their actual electrochemical performance. Galvanostatic potential versus current experiments were performed to indicate the cathode composition with the least polarization. The majority of the cathode structure-compositions were also tested at a constant current of 264 or 87.5 milliamperes while recording the potential-time characteristics of the electrode. All electrodes tested had the same geometric area and an energy capacity of a nominal 14 ampere hours. The tests were designed to run a total 48 or 144 hours assuming a 100% current efficiency. This report is divided into two sections: Task I covers the cathode evaluation and Task II discusses the separator study.

TASK I - CATHODE EVALUATION

A. Cathode Configurations

Five different cathode configurations were proposed for study. The configurations represented a wide range of controlled

surface-to-volume ratios. The five types of structures examined were: (1) cupric oxide and/or cuprous oxide powder of the desired composition pressed at 50 tons per square inch to form a pellet 35 millimeters in diameter, (2) cupric oxide and/or cuprous oxide powder of the desired composition pressed at 50 tons per square inch to form a pellet 35 millimeters in diameter with subsequent sintering at $1,000^{\circ}\text{C}$ for one-half hour in a nitrogen atmosphere, (3) oxidized grid plate structure of the dimensions and physical appearance shown in Figure 1 in Appendix I, (4) oxidized copper needles 0.15 millimeters in diameter by 5 millimeters long. The required quantity of copper needles are placed in an asbestos mold 35 millimeters in diameter and sintered together at $1,000^{\circ}\text{C}$ while at the same time being oxidized, (5) spongy copper electroplated onto a copper screen from a six normal KOH solution. Spongy copper was thermally oxidized under prescribed conditions of atmosphere and temperature to give the desired oxide composition. Further details and discussions are given in Section C of Task I.

B. Copper Oxide Composition

Five different copper oxide compositions were examined. It was felt that this was necessary in order to ascertain the trend in performance characteristics of the different oxides. These oxide compositions are (1) 100% cupric oxide, (2) 75% cupric oxide plus 25% cuprous oxide, (3) 50% cupric oxide plus 50% cuprous oxide, (4) 25% cupric oxide plus 75% cuprous oxide, (5) 100% cuprous oxide.

C. Cathode Preparation Procedure

1. Pressed Powder Cathodes

The required quantity of Fisher reagent grade cupric oxide and/or cuprous oxide was weighed out and placed in a die 35 millimeters in diameter and pressed at 50 tons per square inch. The total quantity of copper oxide used was sufficient to produce a cathode having an energy content of 14 ampere hours. The table below indicates the amount of each oxide needed to give a cathode of the proper composition and energy content.

Table 1

Wt. % CuO	Wt. % Cu ₂ O	g CuO	g Cu ₂ O
100	--	20.79	--
75	25	17.52	5.84
50	50	13.39	13.39
25	75	7.80	23.40
--	100	--	37.40

Several attempts were made to incorporate a small amount of carbon black in the electrode to increase its electrical conductivity. A typical value of the resistance through a 100% cupric oxide pressed powder electrode was 12,000 ohms. Addition of 5, 2 and 1 volume percent of carbon black indicated that any addition less than 5% had no effect in decreasing the electrode resistance. Addition of 5% carbon black produced an electrode having a resistance of 128 ohms. Even though it was possible to decrease the resistance of the electrode, it must also remain

mechanically stable while in the eutectic chloride electrolyte. The electrode was set into 59 mole percent lithium chloride plus 41 mole percent potassium chloride at 427°C for 24 hours. At the end of this time the electrode had completely disintegrated and upon cooling appeared as a black sponge. Due to the results of this test, attempts to decrease the electrode resistance were abandoned. It was found in later tests that after a short time (approximately 1 hour) under current drain, enough copper oxide is reduced to elemental copper to considerably reduce the IR losses in the electrode.

Pressed powder electrodes prepared from 100% cupric oxide, 75% cupric oxide plus 25% cuprous oxide and 50% cupric oxide plus 50% cuprous oxide could be pressed as described above to form mechanically stable cathodes. Attempts to prepare cathodes of the composition 100% cuprous oxide and 25% cupric oxide plus 75% cuprous oxide however, failed. It appears that the particle size of the cuprous oxide powder was too fine (1μ or less) to be coherent at 50 tons per square inch. Consequently, one half pound of cuprous oxide was slugged. The slugging operation consists in pressing the powder at 150 tons/in.^2 , granulating the particles and separating the larger particles. The particles separated were about 30μ . Using the larger particles, 50 tons per square inch was again used in an attempt to produce mechanically stable cathodes of high cuprous oxide content. These cathodes were noticeably stronger than the initial attempts, but still were rather fragile. Immersion in eutectic chloride melt for 24 hours caused a complete disintegration of the electrode pellet.

In order to arrive at some structure in which these two compositions could be electrochemically tested, the powders were packed in a small copper bucket. The mouth of the bucket was then covered with a piece of separator material normally used in the cell during electrochemical testing. To assure that a uniform composition existed throughout these pressed electrodes, the appropriate amount of each oxide was weighed and manually mixed together. The batch was then placed in a one liter screw capped jar along with enough porcelain spheres to nearly fill the jar and placed on a roller mill for 24 hours. The pressed powder cathodes were produced from this powder.

2. Sintered Pressed Powder Cathodes

The initial step used in the preparation of the sintered pressed powder cathodes is exactly the same as the preparation of the pressed powder cathodes. Cathodes prepared to this point are placed in a nitrogen atmosphere and sintered at $1,000^{\circ}\text{C}$ for one-half an hour. Cathodes prepared from 100% cupric oxide, being the exception, are treated similarly but in an air atmosphere. Pure cupric oxide cathodes do not change composition from their initial composition during sintering; weight analysis, however, shows that cathodes initially containing cuprous oxide and cupric oxide change compositions slightly during the sintering process. By weight analysis, it is observed that from 2 to 3 percent of the cupric oxide converts to cuprous oxide during the sintering process.

The sintering process produces cathodes that are considerably stronger than the electrodes prepared by pressing alone.

3. Thermal Oxidation of Copper

The remaining three cathode configurations rely upon the thermal oxidation of the copper to form specific amounts of cupric and cuprous oxides. Samples used to study the thermal oxidation of copper are made from the before mentioned copper needles. An asbestos mold was used to give a circular configuration and the initial specimen weight was 5 grams. The copper needles were sintered together by placing the needles in the mold into a tube furnace at $1,000^{\circ}\text{C}$ for one-half hour in air. The needles and mold were removed from the furnace, cooled and the mold removed. The electrodes were then replaced in the tube furnace to continue the oxidation study. The aim of the method was to completely oxidize the copper needles to cupric oxide in air and later to reduce a portion of the cupric oxide to cuprous oxide. The initial oxidation of the copper completely to cupric oxide was necessary to assure that no elemental copper remained. The proportion of cupric to cuprous oxide formed was determined by weight analysis as given in Section E.

Initial investigation was carried out in the following manner. Three samples were prepared as mentioned above and placed inside a combustion tube at $1,000^{\circ}\text{C}$. Both ends of the tube were kept open to allow free convection of the air. The first sample was removed after 17 hours, the second after 24 hours and the third after 41 hours. Each sample was analyzed giving the following results.

Table 2

Sample	Time at Temp. (hrs)	% Cu ₂ O	% CuO
1	17	30.39	69.61
2	24	18.93	81.07
3	41	16.05	83.95

As shown by weight and chemical analysis, the above samples have been completely converted to one of the oxides. It is seen that a direct heating of the sample at 1,000°C will produce an oxide composition of 75 weight percent cuprous oxide - 25 weight percent cupric oxide. It was hypothesized that the slowness of the formation of the cupric oxide might be due to insufficient flow of air into the combustion tube. In order to ascertain whether insufficient oxygen was present, another set of two copper needle electrodes was prepared as before and both placed in the combustion tube at 1,000°C. Air was forced through the tube continuously at a slow rate (approximately 200 cubic centimeters per minute) for 24 hours. Upon analysis, both samples gave exactly the same results of 4.6 weight percent cuprous oxide - 95.4 percent cupric oxide. After 48 hrs. heating the quantity of CuO is in excess of 99%. Apparently the supply of oxygen was not sufficient in the former case to allow the cupric oxide to form with any rapidity. The remainder of these samples were placed back into the furnace at 1,000°C for 8 and 16 hours in a nitrogen atmosphere. Analysis indicated that the 8 hour heating converted to 17.8 weight percent cuprous oxide - 82.2 weight percent cupric oxide and the 16 hour heating gave 35.1 weight percent cuprous oxide - 64.9 weight percent cupric oxide. These results indicate that copper can indeed be

thermally oxidized to give the desired ratio of cupric to cuprous content. Definite times are not given to convert a certain electrode to cupric or cuprous oxide since it will depend on the physical construction of the electrode. That is to say that an electrode with low porosity will require a longer time to form the oxide than will an electrode having a relatively open structure. The procedure then, that is being used, is to subject several electrodes of the same design to the heating procedure. The electrodes are removed periodically and weighed. If additional heating is required as indicated by the weight change, the heating is continued so that the desired composition is produced. Since the contract does not include a time allotment to fully investigate methods to thermally oxidize electrodes and since it is a very time consuming task, only enough data have been collected to act as a guide in producing the required electrodes. As the required electrodes are made, appropriate results on oxidation time will be collected so that eventually certain conditions can be specified to give a desired cupric oxide to cuprous oxide ratio.

The rate of oxidation of copper needles at 1,000°C in forced air and in oxygen is shown in Figure 2, Appendix I. This graph is to be taken as qualitative since it will apply only to electrodes of the same configuration, density, porosity, etc. as used in this test. From the shape of the curve it is seen that initially a fast oxidation of the copper occurs. This corresponds to a build-up of oxide on the surface of the copper to a point

where further diffusion of the oxygen to the copper is impeded. Another explanation given by Gulbransen, et. al. (1, 2) is that the copper must diffuse through the oxide film before it is oxidized. Either case could explain the shape of the curves.

4. Oxidized Grid Plate Structure

Strips of copper were cut from a 0.01 inch thick sheet to the dimensions of 30 x 18 millimeters. 100 of these were placed together in a jig and slots were milled into the long dimension side. 7 slots 0.5 millimeters x 10 millimeters deep were evenly spaced on this side. 14 of the prepared strips were fitted together forming a grid structure having 36 square holes and having overall dimensions of 2.5 x 2.5 x 1.8 centimeters. The pure copper grid having a nominal weight of 12.6 grams corresponds to an energy content of 10.7 ampere hours if the complete electrode is converted to cupric oxide. These structures are oxidized according to the thermal oxidation procedure given in Section C-3. Before the grids are oxidized they are immersed in 12 normal hydrochloric acid to clean the surface of the copper, rinsed in distilled water and dried at room temperature.

5. Oxidized Copper Needles

Copper needles forming this electrode configuration are 0.15 millimeters in diameter and 5 millimeters long. A mold 35 millimeters in diameter was formed from damp asbestos by forming it around a rubber cylinder 35 millimeters in diameter. This mold

is then thoroughly dried at 100°C and removed from the cylinder. Into this mold is placed a weight of copper needles sufficient to give a 14 ampere hour capacity cathode after oxidation. The quantity of copper used of course depends upon the relative amount of cupric and cuprous oxides desired in the final electrode. The quantity of copper used to produce cathodes of a 14 ampere hour capacity possessing various amounts of copper oxides is given in the table below.

Table 3

W/o CuO	W/o Cu ₂ O	Initial Wt. of Cu (gms)
100	0	16.60
75	25	19.18
50	50	22.58
25	75	27.02
0	100	33.30

The needles in the mold are placed in a furnace at 1,000°C in air for one-half an hour in order to sinter all the particles together. The electrode is removed from the furnace, cooled and asbestos is removed so the oxygen diffusion to the copper is not unduly impeded during the subsequent oxidation. The electrode is oxidized according to the thermal oxidation procedure given previously.

6. Oxidized Spongy Electrode Deposited Copper Cathodes

To prepare a spongy copper deposit an electro-deposition cell was constructed according to the following instructions: a

plastic container 30 centimeters long x 10 centimeters wide x 8 centimeters deep was used as the main body of the electro-deposition cell. The cathodes of this cell were made from 40 mesh copper screen 8 x 10 centimeters in dimension and connected in parallel. The anodes were constructed of 0.6 millimeter thick copper sheet; these also being 8 x 10 centimeters in parallel. The cell contained a total of 8 cathodes and 9 anodes. The current density that was used in all cases was 12 milliamps per square centimeter. This corresponds to a total current of approximately 7 amperes. The electrolyte used for this system was 6 normal potassium hydroxide containing approximately 5 grams of cupric hydroxide in each liter of solution. Current was allowed to flow for approximately 50 hours giving a total of about 25 grams of fluffy copper deposit. This corresponds to roughly a five percent current efficiency. One run as described, produces about enough copper to produce only one electrode. Two such units are set up and run constantly. The evolution of hydrogen at the cathode is the prime electro-reaction, but this evolution is the main reason that spongy copper is obtained. A large volume of spongy copper is produced indicating that a large surface exists per gram of copper deposited. After the deposition is complete, the spongy copper is brushed from the cathodes to the bottom of the electro-deposition cell. The copper is then washed with at least five changes of distilled water through an 8 hour period so that any remaining potassium hydroxide may be removed from the copper. At the end of the cleaning procedure the last

washing is decanted from the container and the copper is allowed to dry at room temperature. Figure 3 in Appendix I shows the physical and electrical set up for this electro-deposition cell.

This spongy copper powder is formed into an electrode structure in much the same way as described for the copper needle electrodes. An asbestos mold is formed 35 millimeters in diameter into which the copper powder is placed. The copper powder and mold are placed in a furnace in air at 900 to 1,000°C for one-half hour to sinter the particles together. After this time the composite is removed from the furnace and the asbestos mold is removed from the electrode. The copper electrode is placed back into the furnace and further oxidized to give the appropriate ratio of cupric oxide to cuprous oxide according to the procedure outlined in Section C-3.

D. Physical Properties of Cathodes

Four basic physical tests were scheduled to be performed on representative samples of each structure-composition combination. The actual surface area that can participate in electrochemical reaction is of greater interest than the obvious projected area of an electrode. The greater the active surface area exposed, the better the voltage one might expect to see at any particular current density. In the high surface to volume type system, concentration polarization would be reduced by a large factor while activation polarization and ohmic drop would be little affected unless only small current densities were drawn from the cell. Ohmic

drop through small pores in an electrode will play a very small part in the initial polarization since active copper oxide near the surface would carry the main burden of the reaction. Only in the case where all the pores are relatively small, the high ohmic polarization occurs due to the copper build up on the outside surface of the electrode. In this case, the reaction will necessarily proceed deeper into the pore to sustain the reaction. Since the resistance in the pores is directly proportional to the depth in the pore of the actual reaction site and inversely proportional to at least a square of the smallest radius in the pore, it is apparent that an appreciable resistance increase can occur if copper build up occurs on the surface of the electrode.

It is important also to determine the solubility of cupric oxide and cuprous oxide in the eutectic melt. Any copper oxide either being suspended in the melt or possibly dissolved in the melt, can migrate through the separator material to the anode, in which case the overall efficiency of the cell would be very much diminished. Due to these considerations, four physical properties appeared evident to measure. These are: (1) B.E.T. surface area by nitrogen adsorption, (2) total porosity, (3) bulk density, and (4) solubility and rate of solution of the oxides in the electrolyte at 800°F (427°C). Arrangements were made with Mellon Institute in Pittsburgh, Pennsylvania to perform the B.E.T. surface area and total pore volume measurements. Since rather specialized equipment is necessary for these determinations, along with properly qualified personnel, it was agreed to subcontract this portion of the

work. Samples of the electrodes for BET tests were sent for analysis but as of the date of this report only a few results have been received by the Catalyst Research Corp. This data will be carried over in the status report dealing with Task 3.

Bulk density measurements have been made by CRC workers on the various electrode configuration-composition combinations and are reported in the following tables. Bulk density is defined by the weight divided by the volume of the cathode in its final prepared condition. This value is given as grams per cubic centimeter.

The method for measuring the solubility and the rate of solution of the different copper oxides is given below. The rate of solution of the various oxides is determined by taking samples at increments of time; the solubility of the particular oxide is indicated when no further change in copper concentration occurs with time. The following method indicates the manner in which the solubility and the rate of solution were determined. An electrode was placed in a 50 milliliter beaker with 74 grams of eutectic chloride. This was then set into a furnace at 800°F (427°C). Approximately 0.5 gram samples of the electrolyte were removed at each 25 hour time period up to a limit of 150 hours. This was done by using a small glass ladle to dip into the electrolyte and remove the sample. The sample was allowed to solidify before it was weighed. The ladle was weighed previous to taking the sample so that the amount of sample could be obtained then by

difference. The sample was dissolved in concentrated hydrochloric acid after which the copper was electroplated from the solution. This gave the total amount of copper that was dissolved in the eutectic for that period of time. The data is given in terms of the grams of the appropriate oxide per 100 grams of eutectic melt. Reference should be made to Section E for the manner in which the sample was analyzed. Tables 4, 5, 6 and 7 are given below and respectively indicate the B.E.T. surface area, total porosity, bulk density and solubility of the cathode material in eutectic electrolyte.

Table 4
B.E.T. Surface Areas (m^2/gm)

Configuration	Composition				
	100% CuO	75% CuO 25% Cu ₂ O	50% CuO 50% Cu ₂ O	25% CuO 75% Cu ₂ O	100% Cu ₂ O
Pressed Powder	0.975	0.965	1.379*	1.050	1.174
Sintered Pressed Powder	0.179	0.148	0.318	0.219	0.298
Grid Plate					
Needles	0.030	0.021	0.024	0.017	0.016

*Measurements show more than a normal scatter. Subject to correction following redetermination.

Table 5
Porosity (% of Total Electrode Volume)

Configuration	Composition				
	100% CuO	75% CuO 25% Cu ₂ O	50% CuO 50% Cu ₂ O	25% CuO 75% Cu ₂ O	100% Cu ₂ O
Pressed Powder	25.5	26.5	25.8	49.3	58.0
Sintered Pressed Powder	30.0	33.6	25.5	51.8	62.7
Grid Plate	74.9	70.4	72.2	69.8	68.3
Needles	66.9	64.8	59.3	56.2	52.2
Spongy Electroplate	80.6	--	--	--	81.0

Table 6
Bulk Densities (gms/cc)

Configuration	Composition				
	100% CuO	75% CuO 25% Cu ₂ O	50% CuO 50% Cu ₂ O	25% CuO 75% Cu ₂ O	100% Cu ₂ O
Pressed Powder	4.77	4.63	4.60	3.09	2.52
Sintered Pressed Powder	4.48	4.18	4.62	2.94	2.24
Grid Plate	1.60	1.73	1.77	1.84	1.90
Needles	2.12	2.21	2.52	2.67	2.87
Spongy Electroplate	1.24	--	--	--	1.14

Table 7
Solubility (g Cu/100 g Electrolyte)

Configuration	Composition		
	100% CuO	75% CuO 25% Cu ₂ O	100% Cu ₂ O
Sintered Pressed Powder	0.18	0.74	0.67
Grid Plate	0.36	0.49	0.69
Needles	0.18	0.61	0.69
Spongy Electroplate	0.20	0.70	0.64

No difference outside of experimental error could be distinguished between samples taken at 25 hours and 144 hours. Consequently, the rate of solution could not be determined since the electrolyte apparently became saturated with copper ions in less than 25 hours.

E. Technique of Analysis for Metallic, Cuprous and Cupric Copper

1. Standardization of Ceric Sulfate Solution

The method for the standardization of the ceric sulfate solution is given in Appendix II.

2. Standardization of Thiosulfate Solution

The method for the standardization of the sodium thiosulfate is given in Appendix II.

3. Determination of Total Dissolved Copper (Electro-deposited)

The method for the determination of the total copper dissolved as cupric ion is given in Appendix II.

4. Determination of Metallic Copper in an Electrode

The cathode or piece thereof was crushed into a fine powder using a mortar and pestle. A sample of the powder was accurately weighed, the sample weight being dependent upon the amount of copper that was expected to be present in the sample. The sample was treated with about 25 milliliters of 12 normal hydrochloric acid in an atmosphere of nitrogen so that oxidation of cuprous ion to cupric ion would be impeded due to the lack of atmospheric oxygen. This treatment causes the cupric oxide and cuprous oxide to go into solution but metallic copper remains unchanged. To ascertain that the metallic copper does not dissolve in 12 normal hydrochloric acid, a weighed strip of 10 mil thick x 2 centimeters x 3.5 centimeters, clean copper was immersed in the acid for 24 hours. After this time the strip was rinsed thoroughly with distilled water, dried in vacuum at room temperature and reweighed. The final weight of the strip was found to be exactly the same as the initial weight. The conclusion drawn was that this indeed is a method and system in which the chemical reaction with metallic copper is nil for this period of time. In other tests using Fisher reagent grade 100 percent cupric oxide and 100 percent cuprous oxide, it was found that these oxides completely dissolve in 12 normal hydrochloric acid. It is apparent that this treatment will yield valid determinations of copper in the presence of cupric and cuprous oxide.

The solution to be analyzed containing dissolved cuprous oxide, cupric oxide and metallic copper is flowed through a fine porous glass fritted filter crucible which had been brought to a constant weight and accurately weighed. The contents of the crucible were rinsed with three 5 milliliter washings of 12 normal hydrochloric acid. The filtrate and washings were collected and retained for the analysis of cuprous and cupric ions as is described later. The crucible and its contents were dried at room temperature (23°C) in a vacuum. The crucible and its contents were weighed and the content of the metallic copper was obtained by difference. A sample calculation of the percent metallic copper in an original electrode follows:

Sample Calculation:

Known Values:

Weight of analyzed sample = w grams

Crucible weight = c grams

Crucible + Cu⁰ weight = y grams

Equation of Calculation:

$$\% \text{ Cu}^0 \text{ in electrode} = 100 \frac{(y-c)}{w}$$

5. Determination of Cuprous Oxide in an Electrode

The filtrate collected in Section E-4 was diluted to an exactly known volume in a volumetric flask using distilled water. An aliquot of appropriate volume (precalculated since

the approximate cuprous oxide content in the sample was known) was pipeted from the bulk solution for analysis. This aliquot was titrated with a standardized ceric sulfate solution according to the reaction:



The titration was done at ambient room temperature since titrations at higher temperatures caused the complication that chloride ions are oxidized to the gas with consequent inaccuracies. Orthophenanthroline ferrous complex was used as the potential indicator. This solution was retained for further analysis of the total copper content of the solution as described in the next section, E-6. A sample calculation showing the method for computing the percent cuprous oxide in an electrode is given below.

Sample Calculation

Known Values:

Normality of ceric sulfate solution = 0.100 N

Volume ceric sulfate titrated = 35.0 ml.

Volume of diluted sample = y liters

Volume of aliquot extracted from y = x liters

Equation of Calculation:

$$\% \text{ Cu}_2\text{O in electrode} = \frac{100(0.100\text{N})(0.035)71.57 \frac{\text{gCu}_2\text{O}}{\text{eq}})y}{(x)(\text{original sample weight})}$$

This method for obtaining the cuprous content of a sample is only approximate since several factors are involved that cause

inaccuracies. In some cases it is very difficult to have the oxide dissolve in the 12 normal hydrochloric acid. Since this is the case and sometimes requires as much as 16 hours for dissolving a small sample of six tenths of a gram, it was found that slight heating would facilitate the rate of dissolution of the oxide sample. However, upon analysis of identical samples that had been heated and not heated, it was found that 50% of the original cuprous oxide had converted to cupric oxide.

Since some cases require as long as 16 hours to dissolve the oxide, another small experiment was performed in order to determine whether cuprous oxide converts to cupric oxide while remaining at room temperature and standing over a period of time. A sample of Fisher reagent grade 100% pure cuprous oxide was dissolved in 12 normal hydrochloric acid and three samples were titrated. The first sample was titrated immediately, the second sample was titrated after one hour and the third sample was titrated after three hours. It was found that the sample titrated after one hour had a cuprous content 20% different than the original sample and also was found that the sample titrated after three hours had changed cuprous oxide content by a factor of 40%. From this information it can be seen that the samples must be dissolved as quickly as possible at as low a temperature as possible and titrated as quickly as possible. Otherwise the samples containing any cuprous oxide will have the tendency to convert to cupric oxide giving inaccuracies and poor determinations.

It can be seen that where an inaccuracy is involved in a titration of the cuprous oxide and since this same solution is used to determine the cupric oxide, then a resultant inaccuracy will also be involved in the cupric oxide determination.

6. Determination of Cupric Oxide in an Electrode

After obtaining the end point for the cuprous going to the cupric titration, the solution was neutralized by adding 15 normal ammonium hydroxide drop-wise until a faint blue color was apparent throughout the solution. 6 normal sulfuric acid was then added drop-wise until the blue color just disappeared; one milliliter in excess was finally added. This procedure adjusted the pH of the solution to the most suitable value for the titration to follow. Four grams of potassium iodide were dissolved in 10 milliliters of water and was added to the copper containing solution. The solution was swirled gently and continuously and immediately titrated with a standardized sodium thiosulfate solution. Thiosulfate was added rapidly until the color of the iodine became indistinct. Three milliliters of starch indicator solution was added and titrated almost to the disappearance of the blue starch color. Two grams of potassium thiocyanate was added and the solution swirled and titrated to its final end point.

The thiosulfate was standardized directly against pure copper as given in Appendix II.

A sample calculation is given below for the calculation of the percent of cupric oxide in the electrode.

Known Values:

Normality of thiosulfate solution	=	0.100N
Volume thiosulfate titrated	=	45.0 ml.

Volume of diluted sample = y liters
Volume of aliquot extracted from y = x liters
Original sample weight = w grams

Equation of Calculation:

% CuO =

$$\frac{[(0.100N)(0.045 \text{ L}) - (0.100N)(0.035 \text{ L})](39.785 \text{ g/eq})(y)(100)}{(x)(w)}$$

Since the total quantity of copper is present in the +2 state for this titration, account is made in the equation to extract that amount of copper that was due to the original cuprous state.

A second method was used also for the determination of the total copper in the solution. This basically was done by electrodeposition at a constant current and is described in detail in Appendix II. Both methods gave equivalent results and both methods were used in order to expedite the analysis.

7. Gravimetric Analysis used in the Thermal Oxidation of Copper

The following method of analysis applies to the copper grid electrodes, the copper needle electrodes and electrodeposited copper powder electrodes.

The proper amount of copper is weighed out to give a 14 ampere-hour capacity electrode for the particular cupric oxide/cuprous oxide ratio desired in the final electrode. By using the gravimetric factor 79.57 divided by 63.57 the weight of the final electrode can be determined when the electrode has been converted completely to cupric oxide. In the case of the copper needles and the electrodeposited copper powder, the samples

are placed in pre-formed asbestos molds. The samples are then placed in a furnace at 1000°C for about one-half an hour in forced air. By this time the copper needles and the electro-deposited copper powder has sintered together enough so that the molds can be removed from the electrodes. The electrodes are then placed back in the furnace at 1000°C in forced air for 24 hours. At this time the electrodes are removed from the furnace and allowed to cool to room temperature. Each of the electrodes are then weighed to determine whether they have been converted completely to cupric oxide. If the weight is not sufficient as required by the above calculations, the electrodes are placed back in the furnace for another period of time. This procedure is repeated until the electrodes have been at least 99% converted to cupric oxide. At this point the electrodes consist essentially of pure cupric oxide. If a pure cupric oxide, that is 100% cupric oxide, electrode is desired, this electrode is then ready for electrochemical testing. For mixtures of cupric oxide and cuprous oxide in the electrode, the percent by weight of each component desired is converted to grams by calculation so that a 14 ampere-hour capacity electrode is produced. Since the conversion of the copper to cupric oxide produces the maximum weight electrode, the conversation of part of this cupric oxide to cuprous oxide will cause a reduction in weight. The electrode is placed in a nitrogen atmosphere at 1000°C for a period

of time depending upon the percentage of cuprous oxide wanted in the final electrode. At this point the electrode is cooled in a nitrogen atmosphere so that removal from this atmosphere does not cause oxidation due to atmospheric oxygen. Again, the electrode is weighed, and is compared to the pre-calculated value desired for this composition electrode. If the weight indicates that too much cupric oxide still exists, the electrode is placed back in the nitrogen atmosphere at 1000°C for another short period of time. If the electrode weight is too low, indicating that too much cuprous has been formed, the electrode is heated in forced air at 1000°C for a short period of time in order to bring the electrode back up to the cupric state which is desired. This procedure can be repeated until the desired electrode composition is achieved. Figure 4 in Appendix I shows the grams of copper necessary to use in order to produce a 14 ampere-hour electrode at a particular composition. Figure 5 in Appendix I shows the final electrode weight that must be achieved in order to attain a particular cuprous oxide to cupric oxide composition.

8. Quantitative Determination of the Solubility of
Copper Oxide in Eutectic Electrolyte at 427°C

A discussion of this topic is given in Section J.

F. Anode (Counter-Electrode) Preparation

The anode was given secondary importance throughout this study. Since magnesium was proposed as the anode to be used in the prototype cell at the end of this investigation, it was thought advisable to use this electrode as the counter-electrode while examining the electrochemical performance of the cathode. In this way any effect on the cathode due to the magnesium anode will be incorporated in the cathode evaluation study.

Magnesium used for the preparation of the anode was quoted as being at least 99.8% pure with specific impurity levels not exceeding the following amounts: total percentage of aluminum, copper, iron, manganese, silicon, and nickel - 0.20. Maximum percent copper 0.05, maximum percent nickel 0.01.

Two methods have been used to prepare these electrodes; one method used magnesium powder and the other utilized magnesium rod. Both methods produced equally satisfactory electrodes. A detailed analysis of the preparation of each type of electrode follows.

1. Anodes Prepared From Magnesium Powder

78 mesh magnesium granules amounting to 6.65 grams (15 ampere-hour) was weighed out into a die 30 millimeters in diameter. The powder was pressed at 20 tons per square inch. This produced an anode that was mechanically strong and appeared as a solid piece of magnesium. A hole was drilled 75 percent of the

way through the face of the electrode and tapped so that a 6-32 x 3 inch steel screw could be attached. A 6-32 nut, previously placed on the screw, was then tightened against the magnesium. This design gave good electrical connection throughout the duration of the electrochemical test.

2. Anodes Prepared from Magnesium Rod

Magnesium rods, 23 millimeters in diameter, were cut so that each piece had an energy content of 15 ampere hours. The electrical connection to the electrode was made in the same manner as described above, i.e., a hole was drilled 75 percent of the way through the electrode through one face, tapped and a 3 inch steel screw set into place and tightened by securing a nut against the magnesium. Figure 6 in Appendix I shows a pictorial representative of the electrode arrangement. In general, the rod was used to prepare the anodes since it is easier and more convenient to handle than is the granulated magnesium powder.

G. Reference Electrode for Half-Cell Testing

The reference electrode used in all the half-cell testing was of the silver-silver chloride type. A 25 ml silver wire was inserted inside a Pyrex tube containing 0.13 M silver chloride in eutectic lithium chloride-potassium chloride. The bottom of the tube was plugged with a mat of vitron fiber and communication was made with the main body of the electrolyte through a small hole in the Pyrex tube. The reference electrode was operated in such a manner that the solvent level inside the tube was the same level as that of the bulk electrolyte in which the reference electrode was being used. Figure 7 in Appendix I shows the physical details of the reference electrode.

H. Electrolyte

Electrolyte used in this study was 59 mole percent lithium chloride - 41 mole percent potassium chloride, i.e., its eutectic composition. The electrolyte was prepared by and obtained from Anderson Physics Laboratory, Inc., Champaign, Illinois. The purity of the electrolyte was determined by polarographic analysis at Anderson. The polarograph cell consisted of a ten mil platinum test electrode and a counter-electrode/reference electrode made from a platinum flag approximately 1 square centimeter in area. A typical polarogram is shown in Figure 8 in Appendix I. As can be seen no wave is apparent in the curve until the chloride ion begins to oxidize to chlorine gas. The only indication of a wave at less than -2.6 volts is a sharp rise due to the chlorine

evolution at about -2.4 volts. In order to quote a residual current at -2.5 volts as requested in the technical proposal, the residual current lying between 0 and -2.0 volts must be extrapolated to -2.5 volts. The value read from the graph at -2.5 volts is a combination of the residual current and the current due to the oxidation of the chloride ion. The polarograms were obtained at 400°C. Nine batches of this salt were purchased and each batch was analyzed separately. The residual currents of each batch is listed below in Table 8.

Table 8

Sample No.	Residual Current at -2.5V (μ A)
182-46	1.0
184-5	0.8
184-21	1.6
184-23	1.4
184-24	2.8
184-25	1.1
184-27	2.5
184-28	1.3
184-30	2.0

Each batch represents one kilogram of salt and all batches are well within the allowed 6 micro-ampere residual current level at -2.5 volts. This salt was used for all the testing in which salt was required.

1. Half-Cell Tests

Two different types of half-cell tests have been performed on these cathodes. Potential versus current data at steady state indicates whether activation, ohmic or concentration polarization is playing an important role in the cathode performance. This data will also indicate whether cupric or cuprous oxide gives a better potential under various current drainings. Potential versus time curves at a constant current allows one to examine the electrochemical performance of an electrode in relation to its physical structure. For instance, an extremely low porosity copper oxide cathode would show a shorter life than a relatively open structure due to the copper reaction product blocking the interior of the electrode. Potential versus time data also allows the utilization to be calculated. The utilization on a particular cathode will be dependent mainly on the cathode structure, effectiveness of the separator and the amount of oxide going into the electrolyte, either by dissolution or by suspension.

1. Potential Versus Current Data at Steady State

Refer to Figure 9 through 12, Appendix I throughout this discussion. The potential versus current data were obtained galvanostatically. The test circuit consisted of a variable 25 ohm resistor and a 0 to 500 milliamp meter in series with the test cell and a vacuum tube voltmeter connected directly between the cathode and the reference electrode (see Figure 13, Appendix I).

The current was set by varying the resistor until the desired reading registered on the ammeter. This current was kept constant for a 10 minute interval at which time the potential of the cathode was read versus the reference electrode. For about the first 6 or 7 minutes after setting the current, the potential would drift but from this time out to 15 minutes no further potential change was noted. Therefore steady state was taken to be at 10 minutes. The cathode was run at 200 milliamps for one-half hour before any E vs. i data was collected. Potentials from which these graphs were obtained at constant currents of 0, 60, 100, 150, 200, 300, 400 and 500 milliamps. All cathodes had a projected geometric surface of 9.6 square centimeters.

Much difficulty was experienced with failures of the furnace during these and the E vs. t experiments. Originally these experiments were conducted in a 50 milliliter Pyrex beaker which set into an upright tube furnace "well" surrounded by exposed heating elements. After a very short period of time enough salt would evaporate and react with the coils so as to cause a coil break. Various methods were employed to isolate the vapors from the coils such as asbestos and mica insulation. However, materials of this nature cause fluctuations in the temperature of the electrolyte as great as $\pm 40^{\circ}\text{C}$. This partially was due to the type of temperature control used. The temperature control senses the temperature through a chromel-alumel thermocouple which in turn activates or de-energizes a relay. With asbestos

or mica shielding the coils, the coil side of the insulation would considerably over-heat. By the time the electrolyte reaches its desired temperature, a large excessive of heat continues to be transferred through the insulation causing the electrolyte to greatly over-heat. It was found that by placing the 50 milliliter beaker containing the cell inside a tall form 200 milliliter beaker, the problem was solved. Heat transfer was much more rapid causing only $\pm 5^{\circ}\text{C}$ variations in the electrolyte while at the same time protecting the coils of the tube furnace. Due to this problem and the time consuming problem of defining the conditions under which copper can be preferentially thermally oxidized to cupric or cuprous oxide, more time was required to perform these tests than had originally been anticipated.

As a point of reference, the magnesium anode has a potential of approximately 1700 millivolts versus the silver-silver chloride reference electrode. All tests were performed at $427 \pm 5^{\circ}\text{C}$. The overall trend from these results indicate that cuprous oxide gives a better cathode potential than cupric oxide for mixtures of the two oxides. Evaluation of the configuration cannot be made on this type of data since the complete run only required about 2 hours to perform. The E vs. t experiments at constant current are a much better source of information for evaluating the most desirable configuration. To obtain the highest cell potential, a cathode made from 100 percent cuprous oxide is recommended. Using a sintered pressed powder cathode as an example,

the table below indicates the comparison of the different cathode compositions at two current levels. These currents represent a proposed 90% utilization of a 14 ampere-hour cathode for 48 hours and 144 hours. In this table it is to be noted that the lowest cathode potential will give the largest cell potential.

Table 9

Selected E vs. I Data - Sintered Pressed Powder

Cathode Composition		E vs Ag/AgCl (mv)	
% CuO	% Cu ₂ O	88 ma	264 ma
100	--	480	672
75	25	426	557
50	50	497	693
25	75	415	480
--	100	482	446

2. Potential vs. Time at Constant Current

Refer to Figures 15 through 53 throughout the discussion of this section. The potential vs. time data was obtained galvanostatically at 264 ma for the 2 day tests and at 87.5 ma for the 6 day tests. The test circuit is shown in Figure 14, Appendix I and consists of a power supply operated at 200 volts, a current regulating variable resistor, an ammeter and a Varian G-14 recorder. The constant current is achieved by using a high voltage power supply having the majority of the potential dropped across a load resistor. This then means that if the test cell

voltage changes, the potential change will allow only a minute current change. For example, if the test cell voltage changes by one volt, the cell current will only change by a factor of 1/200 or 1.3 ma for the two day tests and 0.44 ma for the 6 day tests. Except for the last half hour of a 50 hour test, the half-cell potential changes much less than one volt (about 0.3V).

The cell construction in all cases was the same and is shown cross-cut in Figure 54, Appendix I. The cell case utilizes a 50 ml Pyrex beaker. A circular piece of copper having a current delivery tab is placed on the bottom of the beaker. The copper tab is coated with Sauer-Eisen cement to prevent oxidation. The cathode is placed next into the beaker so that it rests on the copper sheet. On top of the cathode was placed a 1/16" thick piece of vitron that acts as a separator. Salt (59 mole % LiCl + 41 mole % KCl) is melted at 427°C into the cell until 70 gms have been added for tests 70 through 111 while 50 grams was used in tests 1 through 69. The cell is allowed to remain at temperature for one-half hour to allow the salt to displace any air-voids before a test is begun. A calumel-alumel thermocouple encased in a Pyrex well was placed in the electrolyte and acted as the sensor with which the temperature regulator was operated. A reference electrode constructed as shown in Figure 7, Appendix I was placed in the melt at the same time the salt was added so that a reasonable time could be allowed for any equilibration. A magnesium anode was placed in the melt salt so that the spacing between the anode and cathode faces was nine millimeters. In several cases (as noted

Table 10

Pressed Powder Cathodes

Test No.	Test Discharge (hrs)	Cathode Composition (% Cu ₂ O)	Cathode Capacity (Coul/A-hrs)	Mg Anode Capacity at Start (Coul)	Total Mg Anode Consumed (Coul)	Mg Anode Reacted Electrochemically (Coul.)	Cath Life (hrs)	% Effic	% Util	Is.d (ma)
1	48	0	50,000/13.9	>55,600	--	--	5.5	11.3	--	--
4	"	"	50,000/13.9	>55,600	--	--	8.6	17.6	--	--
11	"	"	50,000/13.0	>55,600	--	--	10.3	21.0	--	--
6	"	25	49,780/13.9	>55,600	--	--	7.9	16.2	--	--
25	"	"	49,180/13.7	>55,600	--	--	13.8	28.8	--	--
20	"	50	49,220/13.7	>55,600	--	--	13.6	28.1	--	--
22	"	75	50,490/14.0	>55,600	--	--	26.4	53.5	--	--
21*	"	"	50,490/14.0	>55,600	--	--	6.2	12.6	--	--
24	"	100	50,400/14.0	>55,600	--	--	10.4	21.1	--	--
41	144	0	49,800/13.8	76,500	11,450	5,350	17.0	10.8	46.7	100
44	"	"	50,200/14.0	70,000	16,500	6,800	21.6	13.5	41.2	125
45	"	25	51,200/14.2	71,500	38,000	31,800	101.0	62.1	83.7	17
43	"	50	50,400/14.0	71,100	27,000	21,100	67.0	41.6	78.2	24
46	"	75	50,420/14.0	73,000	18,800	15,100	48.0	30.0	80.3	21
47	"	100	50,400/14.0	71,900	23,250	20,800	66.0	41.4	89.4	10

*Runs failed due to the current carrying lead breaking loose from the cathode or for other undetermined reasons.

* 25 mm electrode spacing.

in the table) an electrode spacing of 25 mm was used. The anode had a coulombic capacity about 30% greater than the cathode in all cases to insure that the anode would not be a limiting factor in the cell performance. The weights of the anode and cathode were found before the test and the anode was again weighed after completion of the test. In the initial tests the anode was not weighed after the tests since analysis of the "spent" cathode was to be made. Cathode analyses gave irreproducible and unreliable results with which to calculate the percent efficiency and utilization. It was found that little error was involved in determining these values from the anode weights and consequently this practice was adopted. All the cathode tests were conducted to a cutoff potential of 1200 mv vs. the Ag/0.13 M AgCl reference electrode; since the magnesium anode has a half-cell potential of 1700 mv against this same reference electrode, the 1200 mv. cathode half-cell potential corresponds to a cell voltage of 0.5 volts. From the potential (E) vs. time (t) curves, the following data was calculated and tabulated. In the tables under the heading "Cathode Composition" it is to be understood that the remainder of the electrode not specified is cupric oxide. The percent efficiency is defined as the coulombs of energy withdrawn from the cathode to the 1200 mv cut-off divided by the original coulombic capacity of the cathode multiplied by 100. The percent utilization, likewise, is defined as the coulombs of energy withdrawn from the cathode to the 1200 mv cut-off divided by the coulombs of magnesium reacted multiplied by 100. The test numbers marked with "*" had electrode spacings of 25 mm while all the remaining electrodes were tested with a 9 mm spacing.

Table 11
Sintered Pressed Powder Cathodes

Test No.	Test Discharge (hrs)	Cathode Composition (% Cu ₂ O)	Cathode Capacity (Coul/A-hrs)	Mg Anode Capacity at Start (Coul)	Total Mg Anode Consumed (Coul)	Mg Anode Reacted Electrochemically (Coul.)	Cath Life (hrs)	% Effici	% Util	Is.d (ma)
8	48	0	50,700/14.1	>55,600	--	--	15.0	32.0	--	--
58	"	"	51,000/14.2	73,000	--	--	31.5	58.8	--	--
59	"	"	49,800/13.8	72,700	40,300	37,500	39.5	75.4	93.2	19
78	"	"	49,200/13.7	73,800	40,300	40,650	42.8	82.5	101	0
29	"	25	49,650/13.8	>55,600	--	--	19.4	38.6	--	--
27	"	50	53,350/14.8	>55,600	--	--	22.8	43.8	--	--
33	"	75	50,150/14.2	>55,600	--	--	38.7	78.9	--	--
40	"	"	48,500/13.5	73,300	--	--	27.5	58.0	--	--
92*	"	"	51,250/14.3	73,700	39,800	38,000	40.0	74.1	95.5	12
83	"	"	48,340/13.4	73,900	31,300	30,000	31.5	62.0	95.8	12
90	"	"	51,100/14.2	73,900	39,880	37,100	39.0	72.5	93.0	20
85*	"	"	49,000/13.6	73,900	12,000	9,610	10.1	19.6	80.1	66
34	"	100	45,000/12.5	>55,600	--	--	33.8	68.9	--	--
84	"	"	43,550/12.1	73,700	18,100	14,250	15.0	32.7	78.7	50
82	"	"	51,000/14.2	73,300	32,600	20,400	21.4	39.8	62.5	159
89	"	"	47,900/13.3	73,800	34,600	19,400	20.4	40.5	56.1	206
91*	"	"	45,350/12.6	73,800	43,100	36,350	38.2	80.2	84.2	50
48	144	0	48,500/13.5	74,900	43,500	20,800	66.0	42.9	47.8	96
86	"	"	49,600/13.8	74,000	51,530	46,400	145.5	93.3	89.9	10
102	"	"	51,200/14.2	75,100	32,200	30,200	96.0	59.0	93.8	6
49	"	25	49,650/13.7	71,500	18,650	16,450	51.6	33.0	88.2	12

Table 11 (Continued)

Test No.	Test Discharge (hrs)	Cathode Composition (% Cu ₂ O)	Cathode Capacity (Coul/A-hrs)	Mg Anode Capacity at Start (Coul)	Total Mg Anode Consumed (Coul)	Mg Anode Reacted Electrochemically (Coul.)	Cath Life (hrs)	% Effic	% Util	Is.d (ma)
51	144	75	42,000/11.7	72,000	43,200	40,850	129.4	96.4	94.5	5
79	"	"	49,980/13.1	72,000	44,400	33,250	105.6	66.6	75.0	29
97	"	"	47,050/13.1	75,900	25,800	18,080	57.5	38.4	70.0	37
50	"	100	50,100/13.9	72,300	43,000	41,500	131.4	82.4	96.5	21
96*	"	"	45,400/12.6	73,500	7,390	1,138	8.4	2.5	15.4	206
101	"	"	44,900/12.4	74,300	35,700	25,200	79.8	56.0	70.5	37
111*	"	"	50,400/14.0	76,200	22,600	19,320	62.0	38.8	85.5	15

Table 12

Copper Grid Cathodes

Test No.	Test Discharge (hrs)	Cathode Composition (% Cu ₂ O)	Cathode Capacity (Coul/A-hrs)	Mg Anode Capacity at Start (Coul)	Total Mg Anode Consumed (Coul)	Mg Anode Reacted Electrochemically (Coul.)	Cath Life (hrs)	% Effic	% Util	Is.d (ma)
26	48	0	10,680/2.96	>55,600	--	--	8.6	78.9	--	123
98	"	"	23,650/6.6	74,600	18,680	12,740	13.4	53.8	68.3	7
99	"	"	23,900/6.6	74,800	17,930	17,500	18.4	73.2	97.5	--
9	"	50	47,530/13.2	>55,600	--	--	34.8	74.9	--	58
67	"	75	25,790/7.2	72,000	24,250	19,900	20.9	77.0	81.9	0
88	"	100	21,400/5.95	80,000	22,540	22,750	24.0	106	101	24
81	"	"	21,300/5.90	75,500	22,500	20,600	21.7	96.7	91.7	66
100	144	0	27,900/7.8	77,100	11,900	6,800	21.6	24.4	57.2	21
108	"	"	25,000/7.0	75,100	19,080	15,420	49.0	61.7	80.9	54
56	"	75	23,500/6.5	70,200	23,250	14,370	45.6	61.6	61.7	14
55	"	100	19,200/5.3	72,700	22,200	19,080	60.6	61.5	85.9	81
68	"	"	19,100/5.3	73,100	23,750	12,280	39.2	64.3	51.7	121
107	"	"	19,000/5.3	74,800	27,400	12,000	35.4	58.6	43.7	163
105	"	"	19,120/5.3	73,500	23,800	8,300	26.4	43.4	34.9	

Table 13

Electrodeposited Copper Cathodes

Test No.	Test Discharge (hrs)	Cathode Composition (% Cu ₂ O)	Cathode Capacity (Coul/A-hrs)	Mg Anode Capacity at Start (Coul)	Total Mg Anode Consumed (Coul)	Mg Anode Reacted Electrochemically (Coul.)	Cath Life (hrs)	% Effic	% Util	Is.d (ma)
62	48	0	27,300/7.6	68,800	20,400	18,420	19.4	67.5	90.3	28
63	"	75	16,990/4.7	72,000	41,900	17,660	18.6	104	42.2	362
66	"	100	15,380/4.3	66,900	17,050	17,000	17.8	110	99.7	0.21
61	144	0	27,650/7.7	72,800	20,400	15,900	50.4	57.7	77.9	25
64	"	75	16,700/4.5	72,400	23,600	7,250	23.0	45.0	30.7	168
65	"	100	13,800/3.8	72,400	23,150	11,150	35.4	79.9	48.2	94

Table 14

Copper Needle Cathodes

Test No.	Test Discharge (hrs)	Cathode Composition (% Cu ₂ O)	Cathode Capacity (Coul/A-hrs)	Mg Anode Capacity at Start (Coul)	Total Mg Anode Consumed (Coul)	Mg Anode Reacted Electrochemically (Coul.)	Cath Life (hrs)	% Effic	% Util	Is.d (ma)
3	48	0	69,900/19.4	>55,600	--	--	44.3	64.6	--	--
19*	"	"	62,500/17.4	>55,600	--	--	11.0	18.0	--	--
77	"	"	48,800/13.6	74,000	29,420	31,800	33.5	65.2	108	--
23	"	25	49,100/13.6	>55,600	--	--	38.4	64.5	--	--
69	"	75	49,780/13.8	74,000	47,100	28,200	29.7	55.9	59.9	176
87	"	"	51,540/14.3	74,000	52,600	45,100	48.0	87.9	86.6	40
94*	"	"	46,000/12.8	74,000	37,400	33,300	35.0	72.4	89.0	32
60	"	100	51,000/14.2	71,000	36,600	31,900	24.9	49.7	86.8	144
80	"	"	51,350/14.3	74,300	46,000	29,760	31.3	58.0	64.6	144
93*	"	"	44,800/12.5	76,400	44,000	38,600	40.5	85.9	87.6	34
57	144	0	49,500/13.8	72,400	38,440	28,000	89.0	56.6	72.8	32
95	"	"	49,500/13.8	71,100	24,300	20,180	64.0	40.7	83.0	17
70	"	"	47,350/13.1	72,400	30,600	19,460	61.8	40.7	63.6	50
71	"	"	47,350/13.1	72,800	33,750	20,700	65.7	43.7	61.4	55
54	"	75	49,950/13.9	65,500	48,400	35,400	112.2	70.6	73.1	32
109	"	"	50,250/14.0	76,000	30,750	23,300	74.0	46.1	75.8	27
53	"	100	50,400/14.0	66,800	51,000	30,950	98.4	62.0	60.6	56
103	"	"	47,900/13.3	76,400	58,000	22,000	69.9	46.0	38.0	142
106	"	"	50,400/14.0	74,000	45,900	38,300	121.8	76.2	83.5	19
110*	"	"	50,400/14.0	74,400	47,500	21,200	67.2	42.1	44.6	108

The self-discharge current ($I_{s.d.}$) is an average value acting as a figure of merit in determining the rate of coulombic loss due to self-discharge. The figure is calculated from the following equation:

$$I_{s.d.} = \frac{\frac{\text{coulombs of Mg Reacted (100-\% Utilization)}}{3600}}{\text{Cathode Life to 1200 mv in Hours} \left(\frac{100}{100} \right)}$$

This figure is particularly useful in determining the effectiveness of the separator. The most desirable value for this figure is, of course, the smallest value attainable.

Referring to Section D, it can be seen that the electrodeposited copper cathodes have a very low bulk density and consequently would require much more volume to attain a 14 A-hr cell than would some of the other types of cathodes such as the sintered pressed powder or copper needle cathodes. Also, it was observed that they are relatively fragile and will erode easily in shock or vibration modes.

Even though the copper grid cathodes show good utilizations, a volume problem exists similar to the electrodeposited copper cathodes. The large electrolyte space available in the grid electrode is not necessary as can be seen from a comparison to the copper needle electrodes. A cathode consisting of 100% Cu_2O and having a 14 A-hr capacity would require a grid of $\sim 25 \text{ cm}^2$ of projected area. This is based upon the grid being 1.6 cm deep using 0.025 cm thick copper sheet and having grid openings of

5 x 5 mm. Roughly, this would double the volume of a similar cell constructed from a copper needle cathode and would yield a pessimistic value for its total watt-hour/pound factor. The grids also are very fragile after oxidation and must be handled with the greatest care.

The pressed powder cathodes produced a weak structure. In the case of 100% Cu₂O and 75% Cu₂O compositions, 50 tons/inch of pressure was not enough to bond the particles into a stable configuration. In order to test these two compositions, the powder had to be placed in a small copper bucket covered by a vitron separator. The electrochemical performance on these electrodes was also inferior to all the other configurations tested.

The sintered pressed powder and needle cathodes show about equal electrochemical performance at both the six and two day rates. The copper needle cathode is much superior in mechanical strength and consequently would be capable of operation in more varied situations, such as in conditions of shock and vibration.

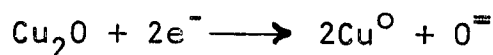
Considering all the variables, we recommend the use of the copper needle cathode as the most effective and reliable structure of the five structures tested.

Literature indicates that cupric oxide is reduced to copper by proceeding through the limiting step $2\text{CuO} + 2\text{e}^- \rightarrow \text{Cu}_2\text{O} + \text{O}^=$ (Jasinski, R., "High Energy Batteries", Plenum Press, N. Y., 1967). Many of our tests also indicate that a pure cupric oxide cathode

operates at 100 to 200 mv greater half-cell potential (lower full-cell potential) than does a 100% Cu₂O cathode under current drain. This would support the suggestion to use a high cuprous oxide content cathode. Further tests also indicate that a 100% Cu₂O cathode has a lower resistance than CuO and thus the potential of the high cuprous oxide cathode stabilizes at its optimum in less than one-tenth the time required to reach the optimum operating potential of a cupric oxide cathode. This is reasonable since it is well known that cuprous oxide is a good semi-conductor. Analysis of our data indicate a considerable overlap of operating potential when using the two extremes of electrode composition. The initial operating potential of a CuO cathode generally is worse than for a Cu₂O cathode. After about one-third of the scheduled operating time, little difference exists in the performance of the two compositions. This may be due to the initial reaction being:



after which the major reaction becomes:



This would explain why we see little overall difference in the overall cell potential in the tests tabulated. From this standpoint either CuO or Cu₂O would be a suitable cathode material with a slight performance edge being attributed to the Cu₂O material. Our recommendation is to use a 100% Cu₂O composition with the copper needle configuration, using copper needles 15 mil in diameter.

J. Solubility of CuO and Cu₂O in 50 Mole % LiCl - 41 Mole % KCl at 427 ± 5°C

The method used for finding the quantity of the various cathode materials suspended as particles or actually dissolved in the eutectic lithium chloride - potassium chloride at 427°C follows. Each of the cathodes were prepared in exactly the same manner as described in the previous sections. Seventy-four grams of high purity Anderson eutectic salt was melted down at 427 ± 3°C in a 50 ml. beaker. The electrodes were inserted in the molten electrolyte and an accumulative time meter was begun. At twenty-five hour intervals, a sample of approximately 0.6 grams of salt was removed with a previously weighed glass ladle. The salt was allowed to freeze in a dry room at less than 3% relative humidity after which the salt and ladle were weighed. The total extracted sample weight was obtained by difference. The sample was dissolved in 100 milliliters of distilled water containing 3 milliliters of 36N sulfuric acid and 1-1/2 milliliters of 16N nitric acid in order to adjust the pH to the proper point. The total amount of copper was plated out electrolytically from the sample. The electroplated copper was carefully washed with water and methyl alcohol and dried at room temperature, and finally weighed. The quantity of copper in the sample was calculated and expressed as grams of copper per 100 grams of electrolyte. The table below gives the quantity of copper found in the electrolyte for three compositions and four configurations of the copper oxide cathodes.

Table 15

Solubility of CuO and Cu₂O

Cathode Composition → Cathode Configuration ↓	100% CuO		75% CuO 25% Cu ₂ O	100% Cu ₂ O	
	$\frac{\text{g Cu}}{100\text{g salt}}$	$\frac{\text{g CuO}}{100\text{g salt}}$		$\frac{\text{g Cu}}{100\text{g salt}}$	$\frac{\text{g Cu}_2\text{O}}{100\text{g salt}}$
Sintered Pressed Powder	0.18	0.23	g Cu/100g salt	0.67	0.75
Copper Grid	0.36	0.46		0.69	0.77
Copper Needles	0.18	0.23		0.69	0.77
Electroplate Copper	0.20	0.25		0.64	0.72

No difference outside of experimental error could be distinguished between samples taken at 25 hours and 144 hours. Consequently, the rate of solution was not determined. The electrolyte apparently becomes saturated with copper ions in less than 25 hours.

It is seen that electrodes having 100% Cu_2O show about three times as much copper in the electrolyte than does a similar electrode made of 100% CuO . According to Klopp, E and Senderoff, S., Second Report NOrd 19240 (December 1958) (AD 226262) the solubility of cupric oxide in this electrolyte is 0.36 gms/100 gms of salt at 600°C ; cuprous oxide solubility is given as 0.42 gms/100 gms salt at 450°C . Neither of these temperatures correspond to our working conditions but give data that can be used as a "rough" comparison. It can be seen from the preceeding table that much more cuprous oxide is present in the electrolyte in our tests. This leads to the conclusion that nearly half of the cuprous oxide is not dissolved but rather exists as Cu_2O particles floating in the electrolyte. Consequently, it appears of the utmost importance to use a separator that has a porosity low enough to keep these particles from reaching the anode. However, a separator most probably can be used that has a relatively open structure and thus will not cause a high internal cell resistance. The vitron separator described in Task II appears to meet these criteria quite well.

Based on weight, the cuprous oxide places about three times as much copper (as either Cu^+ or Cu_2O) in the eutectic electrolyte

as does the cupric oxide (as Cu^{++} or CuO). Based on coulombs, this amounts to ~ 600 coulombs of CuO or ~ 1000 coulombs of Cu_2O lost from the cathode per 100 grams of electrolyte. According to the literature reference given above, the coulombic capacity of the dissolved Cu_2O is only 566 coulombs. The difference of 434 coulombs then must be due to the dislodging of particles from the electrode. In terms of the actual solubility of the oxides, the cuprous oxide would actually cause more self discharge than will cupric oxide. The quantity of dislocated Cu_2O particles from the cathode will be a function of the electrode preparation, i.e., the mechanical stability of the electrode.

K. Cathode Stability Under Dynamic Conditions

Before the reliable recommendation for a final cell could be made in Task 4, it is very important to know whether a particular cathode will stay in tact under various shock, vibration and acceleration conditions. Even though this testing is not required by contract, CRC has felt that this information must be known in order to recommend a proper final design. Because of this we have selected a few specific cathodes that seem promising electrochemically to be tested under dynamic conditions at our own time and expense.

The test container used in these dynamic tests was a cylindrical can, 1-5/8" in diameter by 2" high made from stainless steel. The test electrode was placed in the bottom of this can. On top of the electrode was placed an eight-mesh copper screen in a nickel

collar and the collar spot-welded to the can. This was done to keep the cathode in place and to simulate the conditions of a working cell. A total of six tests was conducted. Four of the containers were filled with molten eutectic chloride salt and allowed to solidify. Each can contained a 100% cuprous oxide cathode. Four configurations were tested including the copper needle electrode, the copper grid electrode, the sintered pressed powder electrode and the electroplated copper cathode. Two additional tests were conducted having the can filled with glycerin in place of eutectic chloride. This was done to test the dynamic capabilities of the cathodes in a simulated operating condition in molten eutectic chloride. Two configurations were tested, the sintered pressed powder cathode and the needle cathode, both being of 100% cuprous oxide composition. Finally a header was placed on the can so that no air space remained inside, and welded. Tests on each one of these containers and cathodes were made under the following conditions:

1. Shock, half-wave, three shocks in each of three perpendicular directions, six axes at 18G for 12 milliseconds.
2. Vibration, sinusoidal 5 to 16 cycles per second at 0.368" displacement, 16-2,000 cycles per second at 5G.
3. Acceleration, 7G in the longitudinal direction, 3G in the longitudinal direction, 4.5G in the lateral direction X_1 X_2 Y_1 and Y_2 .

After these tests the cells were carefully cut open and the cathode was examined. In all of these tests no resonant modes were observed in the test spectrum.

The results of the tests conducted with solid eutectic chloride are: sintered pressed powder cathode - no deterioration; copper needle cathode - no deterioration; copper grid cathode - corner breakage; electroplated copper cathode - heavy erosion. The results of the cathodes tested in the glycerin solution are as follows: copper needle cathode - slight erosion; sintered pressed powder cathode - medium erosion. It is concluded from these tests that copper needle electrodes have the best ability to withstand any dynamic conditions.

TASK II - SEPARATOR STUDY

A. Selection of Separator Materials

Five types of separator material were selected to be examined for stability in 59 mole % LiCl + 41 mole % KCl at 427°C (800°F) and for its ionic conductivity in the same electrolyte.

These materials were:

1. Asbestos
2. Woven glass
3. Fiberfrax
4. Vitron
5. Porous porcelain

The following tabulation provides a specific description of each material:

1. Asbestos
 - a. thickness ---- 40 mil
 - b. % porosity --- 53%
2. Woven Glass
 - a. thickness ---- 7 mil
 - b. % porosity --- 90%
 - c. purchase specifications ---- number Y-1140,
Form 5, Class C, Type ECC-B
 - d. square weave ---- 32 threads/inch
 - e. close weave
3. Fiberfrax
 - a. thickness ---- obtained as bulk (similar to
absorbent cotton) and sliced to desired thickness.

- b. % porosity ---- 67%
- c. purchase specifications ---- Carborundum
Fiberfrax No. 970-F

d. chemical composition:

Al_2O_3 ----- 51.2% max

SiO_2 ----- 47.1

B_2O_3 ----- 0.6

Na_2O ----- 0.6

Total MgO , CaO , Fe_2O_3 ----- 0.5

Binder and other organics --< 0.8

4. Vitron

- a. thickness ---- obtained as bulk (similar to
absorbent cotton) and sliced to desired thickness.
- b. % porosity ---- 87%
- c. purchase specifications ---- Vitron "E" Glass
Microfibers, 0.20 to 0.499 micron fiber diameter,
Johns-Manville Code 104E Glass

d. chemical composition:

SiO_2 ----- $54.3 \pm 0.6\%$

B_2O_3 ----- 7.9 ± 0.4

R_2O_3 ----- 14.8 ± 0.4

$\text{Na}_2\text{O} + \text{K}_2\text{O}$ ----- 0.5 ± 0.2

CaO ----- 17.5 ± 0.4

MgO ----- 5.0 ± 0.4

5. Porous Porcelain

- a. thickness ---- 79 mil
- b. % porosity --- 82%
- c. chemical composition --- unavailable

B. Compatibility of the Separators with the Electrolyte

The first examination that was conducted with the separator materials was designed to determine whether they were chemically and physically stable in the 59 mole % LiCl + 41 mole % KCl electrolyte at 427°C for a period of 200 hours. This must be the first criterion that must be fulfilled in the examination leading to the useful selection of a separator material.

In all these tests, "test strips" of the separator material were cut 7×2 cm. of which 4 cm. (8 cm^2) was allowed to dip into the eutectic electrolyte while maintaining the electrolyte temperature at $427 \pm 5^{\circ}\text{C}$. Four strips of each material were suspended in a 50 ml beaker by a fine piece of nichrome wire which never came in contact with the electrolyte. The "test strips" were weighed previous to their immersion in the electrolyte. One of the four "test strips" was removed from the melt at ~ 50 hour intervals, washed, dried and again weighed. The weight loss or gain and its physical appearance was noted. Each "test strip" was washed by placing it in 250 ml of water for five minutes and repeating this for at least five washings. The sample was then placed on a watch glass and dried for one-half hour at 150°C .

A test was conducted on asbestos to determine whether one-half hour at this temperature was sufficient time to completely dry the

sample. After washing a sample of the asbestos it was dried as noted and weighed. The sample was placed back in the oven for an additional 64-1/2 hours after which it was weighed again. It was found that only a 0.3 mg. weight difference occurred and consequently all remaining tests were dried for 1/2 hour at 150°C.

Tables 16 through 20 below follow the progress of the weight change of the various separator materials throughout the life of the test.

Table 16

Stability of Asbestos in Eutectic Melt at 427°C

Time (Hrs)	Beginning Weight (gms)	Final Weight (gms)	Weight gain(+)/loss(-) (gms)	Wt. Change/cm ² (mg/cm ²)
26.6	0.9771	1.0013	+0.0242	+3.0
93.1	.9197	.8821	-0.0376	-4.7
145.1	.9407	.9278	-0.0129	-1.6
200.0	.9554	.9635	+0.0081	+1.0

In all cases the section of the "test strip" immersed in the melt gave a very white and clean appearance after washing. The strip was not brittle but would not tolerate bends greater than about 20° without cracking. The results show that no effect can be attributed to its chemical stability due to its exposure to the melt. The weight increases noted are probably due to incomplete washing even after five washes. In all cases small particles of the asbestos are seen floating in the wash water.

Table 17

Stability of Woven Glass in Eutectic Melt at 427°C

Time (Hrs)	Beginning Weight (gms)	Final Weight (gms)	Weight gain(+)/loss(-) (gms)	Wt. Change/cm ² (mg/cm ²)
50	0.2291	0.2251	-0.0040	-0.61
100	0.2086	Crumbled	--	--
116	0.2310	0.2276	-0.0034	-0.52
180	0.2194	0.2115	-0.0079	-1.20
Test #2				
48	0.2068	0.2023	-0.0045	-0.64
138	0.1920	Crumbled	--	--
187	0.2176	Crumbled	--	--
236	0.2134	Crumbled	--	--

As noted in the above table, four of the eight glass strips tested became quite fragile and would crumble with the least handling. Another test was attempted by completely immersing the samples in the eutectic. It was thought that the glass strip being partially exposed to the heated air may have caused some reaction with the glass strips. This run had to be discontinued after 50 hours since all the samples had fused to the side of the Pyrex beaker. This indicates that the air was not instrumental in causing the crumbling of the sample but rather that the molten salt was attacking the "test strip". To support this conclusion, it should be noted that all the glass strips lost weight in the first run, the 180 hour strip losing more weight than the 50 hour

sample. The woven glass remains intact while in the melt but becomes very fragile with little mechanical integrity after being in the melt for 100 hours. It appears that the slightest vibration would cause the woven glass strip to disintegrate.

Table 18

Stability of Fiberfrax in Eutectic Melt at 427°C

Time (Hrs)	Beginning Weight (gms)	Final Weight (gms)	Weight gain(+)/loss (-) (gms)	Wt. Change/cm ² (mg/cm ²)
24	0.7826	0.7414	-0.0412	-10.9
90	0.8012	0.7867	-0.0145	- 3.8
144	0.7678	0.7300	-0.0378	-10.1
192	0.8482	--	--	--

At the 192 hour level, it was found that the fiberfrax had completely disintegrated into a pulp throughout the molten eutectic. This indicates that fiberfrax would be an unacceptable separator for our 200 hour cell tests. Even though the fiberfrax does form a pulp, it might still act as a separator but would require the cell to be operated in a fixed position so that the pulp would not settle to one side or the other allowing a portion of the cell to be without any separator. In general this would lead to an objectionable design.

Table 19

Stability of Vitron in Eutectic Melt at 427°C

Time (Hrs)	Beginning Weight (gms)	Final Weight (gms)	Weight gain(+)/loss(-) (gms)	Wt. Change/cm ² mg/cm ²
50	0.3724	0.3483	-0.0241	-3.46
141	0.3598	0.3383	-0.0215	-3.08
190	0.3776	0.3501	-0.0275	-3.94
215	0.3150	0.2966	-0.0184	-2.64

The vitron samples did not change in appearance and were still mechanically strong at the end of the testing period. By weighing it was found that the samples lost from 5.8% to 7.3% by weight and this weight loss was independent of the time the samples remained in the melt. For instance, after a piece of vitron was in the melt 50 hours, it had lost 6.5% by weight; after 141 hours, 6.0%; after 190 hours, 7.3%; and after 215 hours, 5.8%. This indicates that some soluble species in the vitron is being leached from the sample in a relatively short time and no further detrimental effect is observed throughout the course of the 200 hour period. Of the separators tested, this one has the best resistance to any effect the eutectic chlorides may have and from this standpoint, it would be the most suitable separator for use in the thermal cell.

Table 20

Stability of Porous Porcelain in Eutectic Melt at 427°C

Time (Hrs)	Beginning Weight (gms)	Final Weight (gms)	Weight gain(+)/loss(-) (gms)	Wt. Change/cm ² mg/cm ²
66	5.2506	5.2383	-0.0123	-0.98
114	4.0494	4.0233	-0.0261	-2.07
162	5.3714	5.3595	-0.0119	-0.95
233	5.3583	5.3423	-0.0160	-1.27

The porous porcelain appears to be chemically stable in this electrolyte system. After the 233 hour test the sample was still mechanically strong with good porosity. The physical appearance of the 66 hour test showed a uniform gray color on the material while all the remaining tests gave samples that were a mottled gray and white.

From the tests made on the chemical and physical stability of these separators, the following table indicates their usefulness for 50 and 200 hour tests. These conclusions, combined with the conclusions from the next section (Section C), will provide the information upon which a separator will be selected for use in the test cells.

Table 21

Comparison of Separator Materials

Material	Suitable for 50 Hr. Tests	Suitable for 200 Hr. Tests
Asbestos	Yes	Yes
Woven Glass	Yes	No

Continued

Table 21 - Continued

Material	Suitable for 50 Hr. Tests	Suitable for 200 Hr. Tests
Fiberfrax	Yes	No
Vitron	Yes	Yes
Porous Porcelain	Yes	Yes

Even though asbestos sheet was essentially chemically inactive for 200 hours, it is on the verge of becoming an incoherent pulp. For the 50 hour tests, asbestos sheet should be satisfactory but for the 200 hour tests it appears to be marginal.

Vitron and porous porcelain, at this point in the study, appear to offer the best characteristics as a separator material. In the case of vitron, its relatively large pore volume would not seem to be hindered by a high resistance buildup during the cell operation. However, vitron does have a vast network of fibers that will prevent the excessive migration of copper oxide particles to the anode.

C. Separator Resistance

The specifications of this contract require that the AC resistance contributed by each separator material be measured at the beginning and termination of a 200 hour soaking period in 59 mole % LiCl + 41 mole % KCl electrolyte at 427°C (800°F). For this work a General Radio Conductance Bridge was used at 1000 cps.

Since the change of resistivity of the separators is to be measured over a 200 hour period, it was required that the conductivity of the eutectic chlorides does not change over this period; or if it does, it must be determined in what fashion it changes. Figure 55, Appendix I shows the experimental arrangement used in this determination. It was found that the resistance of the melt remained constant over this period of time and the average deviation from the mean was $\pm 3\%$.

This shows that the eutectic chloride electrolyte's resistance is invariant with time over the 200 hour period and consequently will not cause any systematic error when determining the resistances of the individual separators.

A theoretical and experimental treatment presented by Meredith and Tobias, J. Electrochem. Soc., 112, 1257 (1963) allows the resistance of a separator to be calculated if its open space to solid ratio and the conductivity of the electrolyte is known. These calculations indicated that our particular separators would have a resistance of about 0.3Ω . Even though our separators do not strictly adhere to the assumption of Tobias, et. al., the calculation was useful in determining the general magnitude of the resistance that could be expected.

This then imposes a serious restriction on the experimental apparatus. The conductivity bridge (described previously) has an accuracy of $\pm 1\%$. This means that the conductivity cell used must

have a resistance in the vicinity of 1 ohm using only the LiCl-KCl eutectic. As an illustration let us assume a conductivity cell has been constructed having a resistance of 1.00 ohm but on measurement shows 1.01 ohm (the + 1% accuracy). Then if a separator is inserted in the cell having an inherent resistance of 0.22 ohm the instrument might read as low as 1.21 ohm. Upon subtracting this would give a measured value of 0.20 ohm for the separator, or be in actual error by 0.02 ohm. This will give us a value that is only $\pm 10\%$ reliable. It is felt that this illustration would more clearly justify the reason for using a conductivity cell with a low resistance.

After a number of attempts to construct a cell with these principles, one was made that did not leak and was convenient for our use. Essentially, it consists of a nonporous ceramic plate with a "V" slot cut from it. On both sides of the plate a strip of magnesium is placed and held together by pressing between two insulated heated platens. The ceramic plate contains a shallow slot in which the separator can be inserted without increasing the distance between the magnesium electrodes. The open end of the "V" slot allows the electrolyte level to be maintained and observed easily. The area of the separator exposed in the cell was 3.63 cm². Figure 56, Appendix I shows the physical construction of this test cell.

The resistance of asbestos, woven glass, fiberfrax and vitron versus time is shown in Figure 57, Appendix I. The vitron and

fiberfrax samples examined were 62 mils thick while the other materials had a thickness as noted in Section A. The table below is an attempt to compare the resistivities of each material on the basis of a uniform thickness. In the case of the woven glass the table is somewhat misleading since the test was terminated after approximately 40 hours due to the disintegration of the separator.

Table 22
Separator Material Resistance

Material	Thickness (mils)	R (Ω /mil)
Asbestos	40	6.76×10^{-3}
Woven Glass	7	66.5
Fiberfrax	62	5.74
Vitron	62	2.42
Porous Porcelain	79	5.06

From this table a preliminary evaluation can be made on the basis of resistance alone. The three materials that showed the lowest resistance were vitron, porous porcelain and fiberfrax respectively. Porous porcelain would not yield any reliable or consistent resistance measurements. The resistance measured was high throughout the test but showed fluctuations of $\pm 100\%$ of its average value of 2Ω . It appeared that the eutectic chloride could not penetrate the pore structure uniformly. Of the remaining four separator

materials tested, only two showed a constant resistance over the two hundred hour period, i.e., fiberfrax and vitron. Both of these materials gave an initial high resistance: fiberfrax 0.42Ω and vitron 0.68Ω . This appears due to incomplete saturation of the separator at the beginning of the test. In an actual cell this initial high resistance can be eliminated by prefusion of the salt with the separator immersed in it. Fiberfrax also has the tendency to become pulpy and lose its intended configuration after 200 hours in the eutectic as described previously in the stability testing results. Vitron has a slight tendency to swell in the eutectic but remains mechanically sound. Asbestos and woven glass develop cracks and tend to disintegrate in the early part of the testing (~ 20 -40 hours).

Considering the results of the stability testing in Section B and the resistance experiments discussed in this section, it must be concluded that vitron offers the best choice as a separator for this cell system.

CONCLUSIONS

1. Copper needle cathodes gave the most mechanically stable cathode configuration and better or equal electrochemical performance than the other configurations.
2. E vs. t experiments show considerable overlap of data for either 100% CuO or 100% Cu₂O cathode compositions. E vs. t experiments, however, indicate that 100% Cu₂O cathode are 100 - 150 mv less polarized than 100% CuO cathodes.
3. Pressed powder cathodes are very fragile and rupture easily; sintered pressed powder cathodes are nearly as strong as the needle electrodes but do show some erosion in environmental testing. The electrochemical performance is equivalent to the needle cathodes; copper grid cathodes are an impractical design for scale-up; electrodeposited copper is formed in a highly inefficient manner. Electrodes prepared from this material are fragile do not withstand environmental tests and show inferior performance in electrochemical testing.
4. A procedure has been developed by which copper can be preferentially thermally oxidized to CuO, Cu₂O or defined mixtures.
5. B.E.T. surface area measurements of the cathode do not correlate with electrochemical data. Therefore, it is suggested that fine pores in the cathode do not appreciably contribute to the reduction. Rather, it appears that macro-pores contribute the majority of the current.

6. High porosity cathodes perform better than low porosity cathodes; likewise, low bulk density electrodes perform better than high bulk density.
7. Results show that the weight of Cu_2O and its coulombic capacity is greater than for CuO in solution or as suspended particles. Cupric oxide cathodes would be expected to give lower average cell self-discharges.
8. Volumetric analyses for dissolved Cu^{++} and Cu^+ are unreliable as described in this report.
9. The method used to connect the Mg anode to the current delivery lead (Figure 6, Appendix I) was reliable. No cell failures could be attributed to a disconnect of the anode lead.
10. Satisfactory Mg anodes can be prepared by pressing Mg powder at 50 tons/in.² or from Mg rods.
11. Copper needle cathodes of a 14 A-hr capacity, 3.5 cm in diameter indicate that an 80-90 percent efficiency and 40-80% utilization can be achieved. It is expected that improved separator construction will increase these values.
12. The copper needle cathodes were the most stable during the dynamic tests of shock, acceleration and vibration.
13. Vitron E was shown to be stable in molten eutectic for 200 hrs. at 427°C.

14. Vitron E showed the lowest resistance, $2.42 \times 10^{-3} \Omega / \text{mil}$, (measured at 1000 cps at 427°C in molten eutectic) per unit thickness of all the separators tested.
15. Vitron E is the most satisfactory separator examined and is recommended for use in the final cell design.

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	16	E vs. t Data, 2-Day Rate, Pressed Powder Cathodes
	17	E vs. t Data, 2-Day Rate, Pressed Powder Cathodes
	18	E vs. t Data, 2-Day Rate, Pressed Powder Cathodes
	19	E vs. t Data, 2-Day Rate, Pressed Powder Cathodes
	20	E vs. t Data, 6-Day Rate, Pressed Powder Cathodes
	21	E vs. t Data, 6-Day Rate, Pressed Powder Cathodes
	22	E vs. t Data, 6-Day Rate, Pressed Powder Cathodes
	23	E vs. t Data, 6-Day Rate, Pressed Powder Cathodes

- 24 E vs. t Data, 6-Day Rate, Pressed Powder Cathodes
- 25 E vs. t Data, 2-Day Rate, Sintered Pressed Powder Cathodes
- 26 E vs. t Data, 2-Day Rate, Sintered Pressed Powder Cathodes
- 27 E vs. t Data, 2-Day Rate, Sintered Pressed Powder Cathodes
- 28 E vs. t Data, 2-Day Rate, Sintered Pressed Powder Cathodes
- 29 E vs. t Data, 2-Day Rate, Sintered Pressed Powder Cathodes
- 30 E vs. t Data, 6-Day Rate, Sintered Pressed Powder Cathodes
- 31 E vs. t Data, 6-Day Rate, Sintered Pressed Powder Cathodes
- 32 E vs. t Data, 6-Day Rate, Sintered Pressed Powder Cathodes
- 33 E vs. t Data, 6-Day Rate, Sintered Pressed Powder Cathodes
- 34 E vs. t Data, 2-Day Rate, Copper Needle Cathodes
- 35 E vs. t Data, 2-Day Rate, Copper Needle Cathodes
- 36 E vs. t Data, 2-Day Rate, Copper Needle Cathodes
- 37 E vs. t Data, 2-Day Rate, Copper Needle Cathodes
- 38 E vs. t Data, 6-Day Rate, Copper Needle Cathodes
- 39 E vs. t Data, 6-Day Rate, Copper Needle Cathodes
- 40 E vs. t Data, 6-Day Rate, Copper Needle Cathodes
- 41 E vs. t Data, 2-Day Rate, Copper Grid Cathodes
- 42 E vs. t Data, 2-Day Rate, Copper Grid Cathodes
- 43 E vs. t Data, 2-Day Rate, Copper Grid Cathodes
- 44 E vs. t Data, 2-Day Rate, Copper Grid Cathodes
- 45 E vs. t Data, 6-Day Tests, Copper Grid Cathodes
- 46 E vs. t Data, 6-Day Tests, Copper Grid Cathodes
- 47 E vs. t Data, 6-Day Tests, Copper Grid Cathodes
- 48 E vs. t Data, 2-Day Tests, Electrodeposited Copper Cathode
- 49 E vs. t Data, 2-Day Tests, Electrodeposited Copper Cathode
- 50 E vs. t Data, 2-Day Tests, Electrodeposited Copper Cathode
- 51 E vs. t Data, 6-Day Tests, Electrodeposited Copper Cathode
- 52 E vs. t Data, 6-Day Tests, Electrodeposited Copper Cathode

- 53 E vs. t Data, 6-Day Tests, Electrodeposited copper cathodes
- 54 Half-Cell Construction
- 55 Measurement of the Resistance of LiCl/KCl
Over a 200 Hour Period
- 56 Separator Resistance Cell
- 57 Separator Resistance vs. Time

APPENDIX II - Analysis Procedures

- I Preparation and Standardization of Ceric Sulfate
Solution.
- II Preparation and Standardization of Thiosulfate
Solutions.
- III Electrolytic Determination of Copper

APPENDIX I
CIRCUIT DIAGRAMS AND FIGURES

Figure 1
Construction of Copper Oxide Grid Electrode
0.010" Cu Sheet

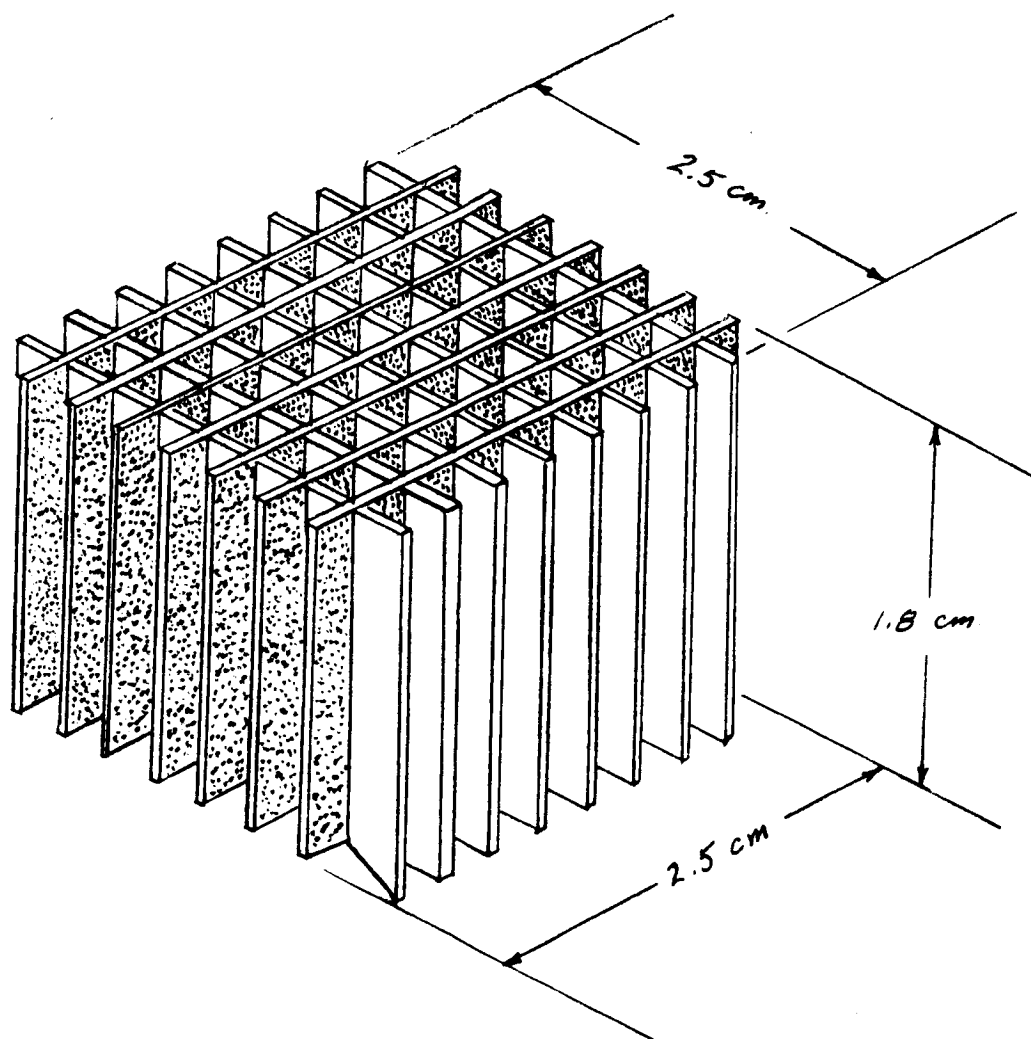


Figure 2

Weight Gain of 25 gm Cu - Needle Electrode at 1000°C

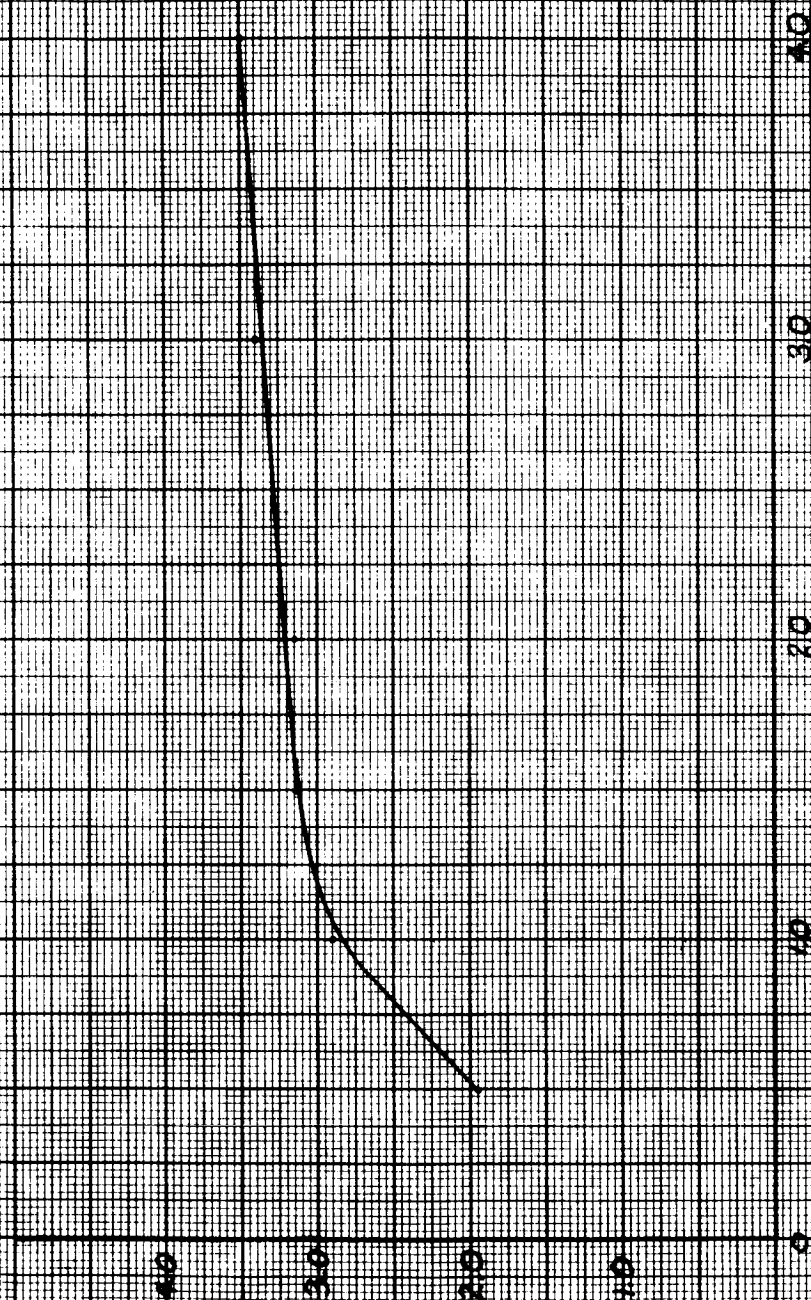


Figure 3
Electrodeposition of Copper Powder
 Current Density = 12 ma/cm^2

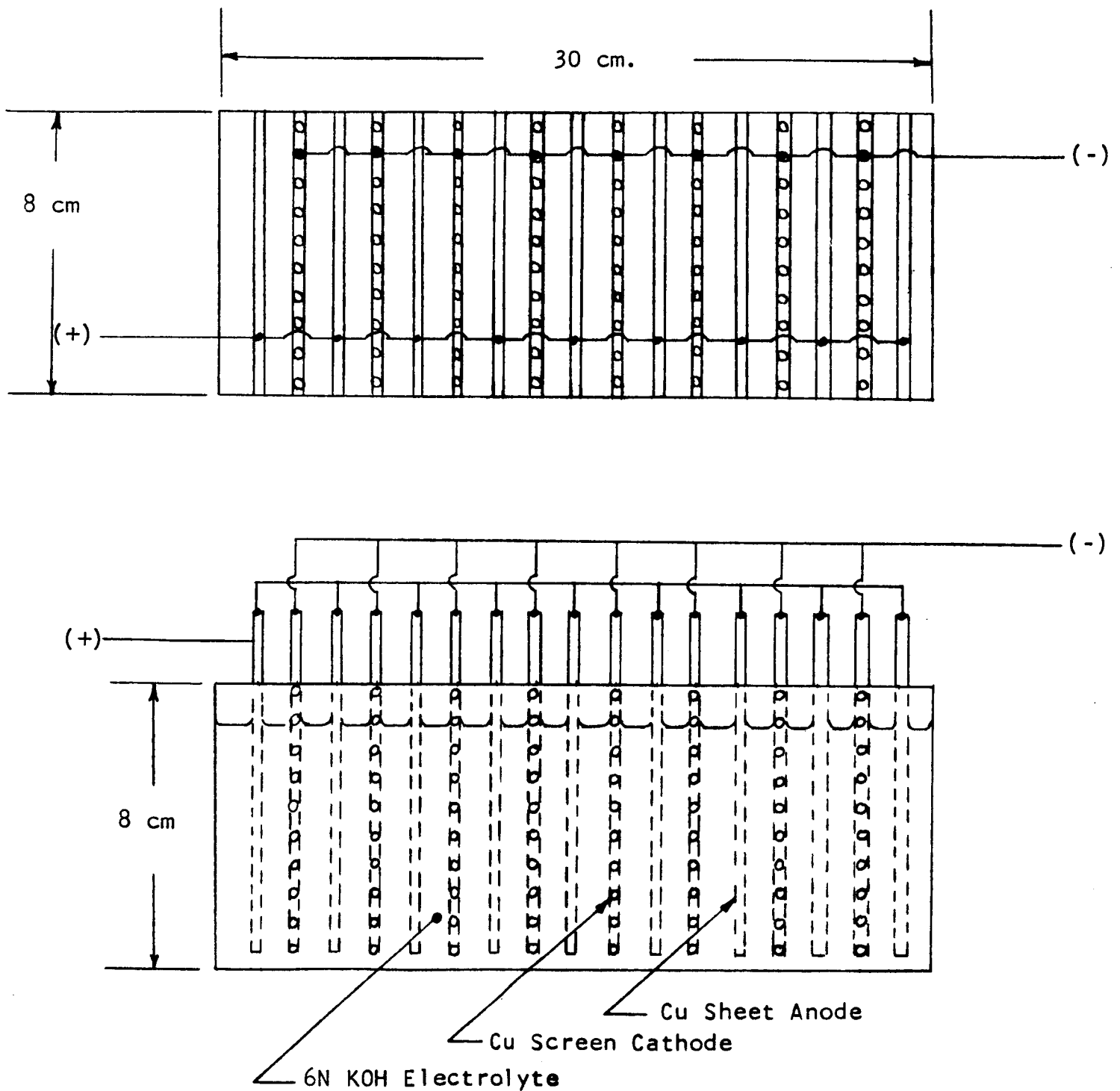


FIG 4

Grams Cu Required to Give a 14 A-Hr Cathode

Weight Percent CuO

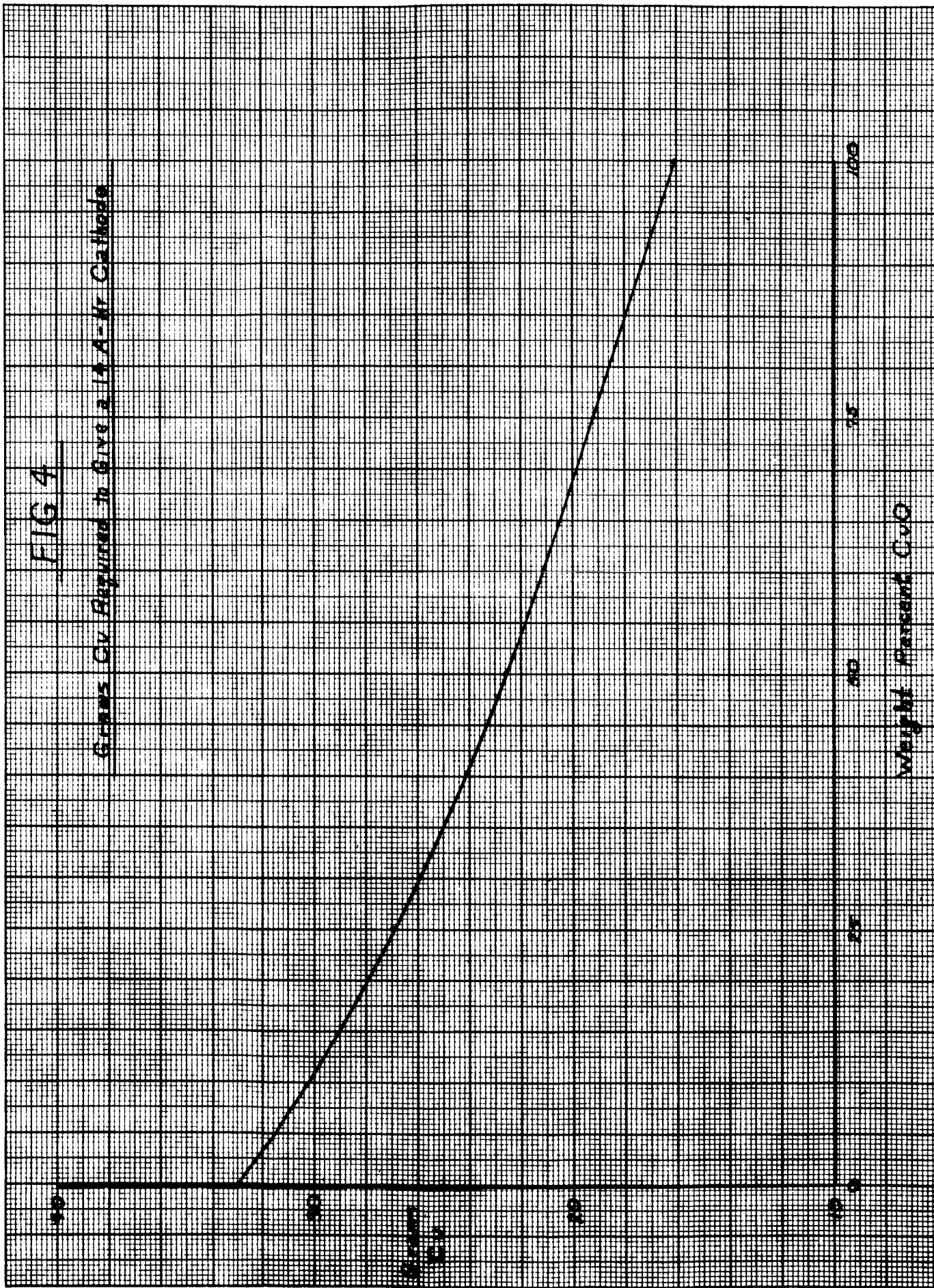


Figure 5

Electrode Weight Required to Produce a 14 A-hr
Electrode at a Specific Composition

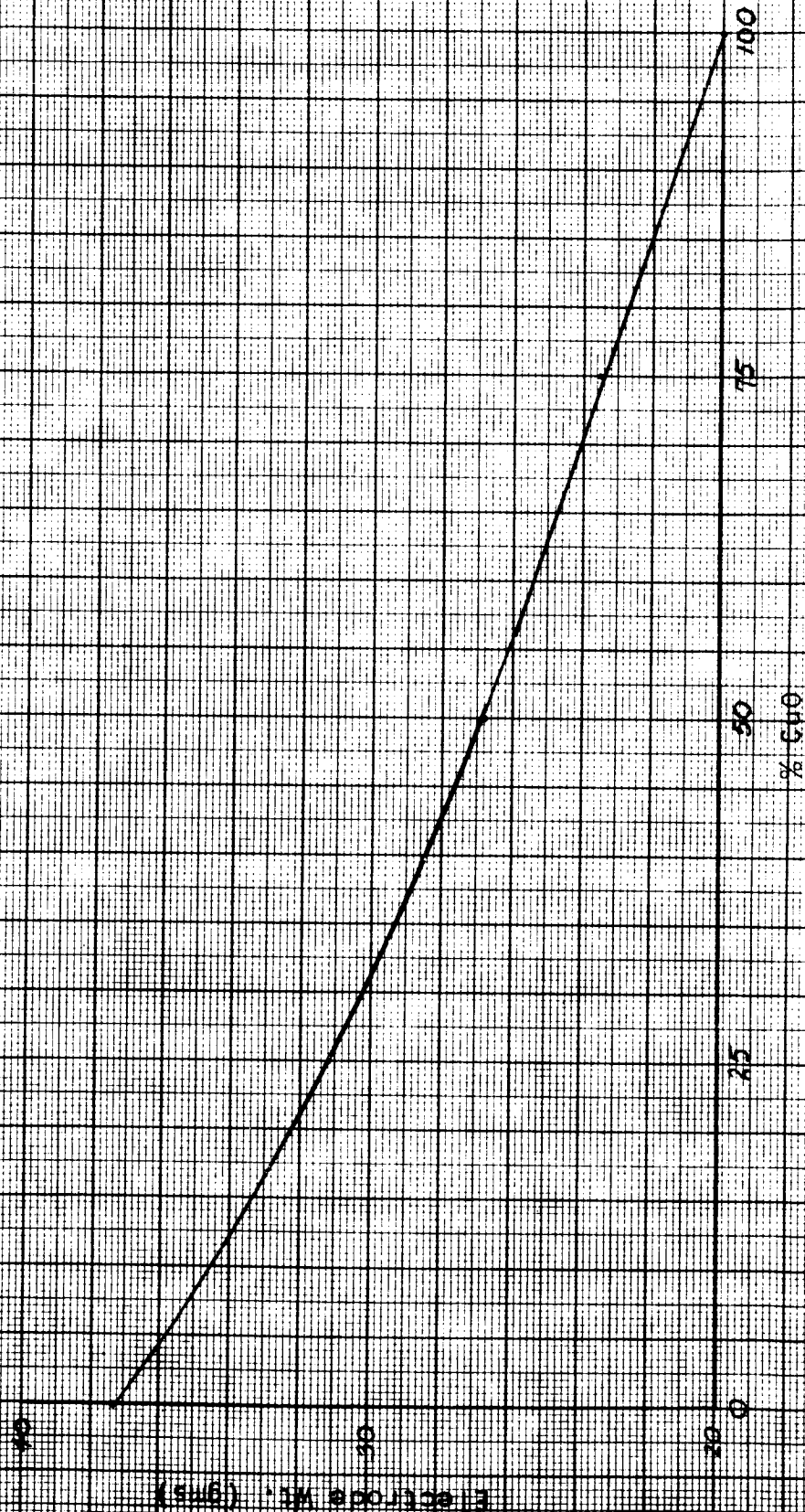
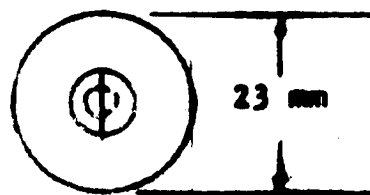
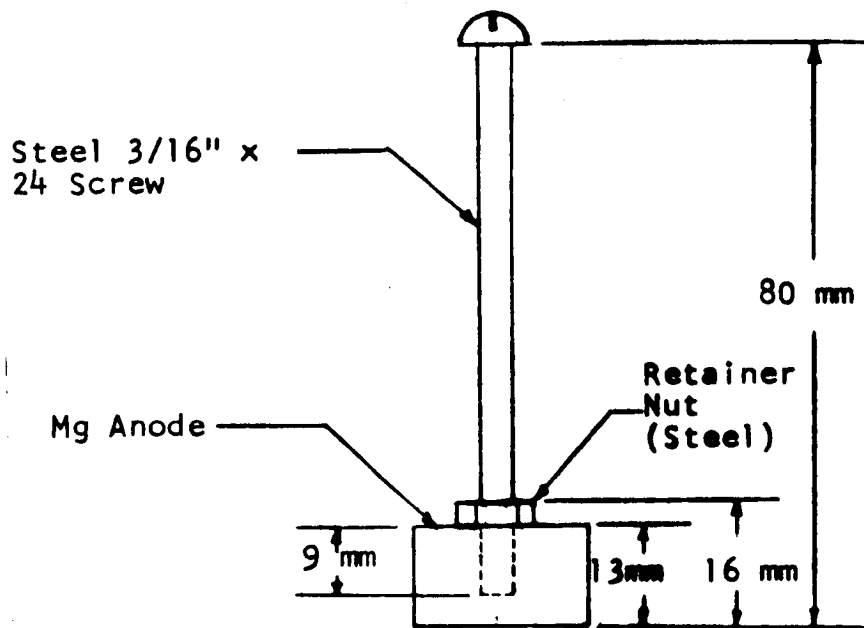


Figure 6
Mg Anode Construction



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Figure 7

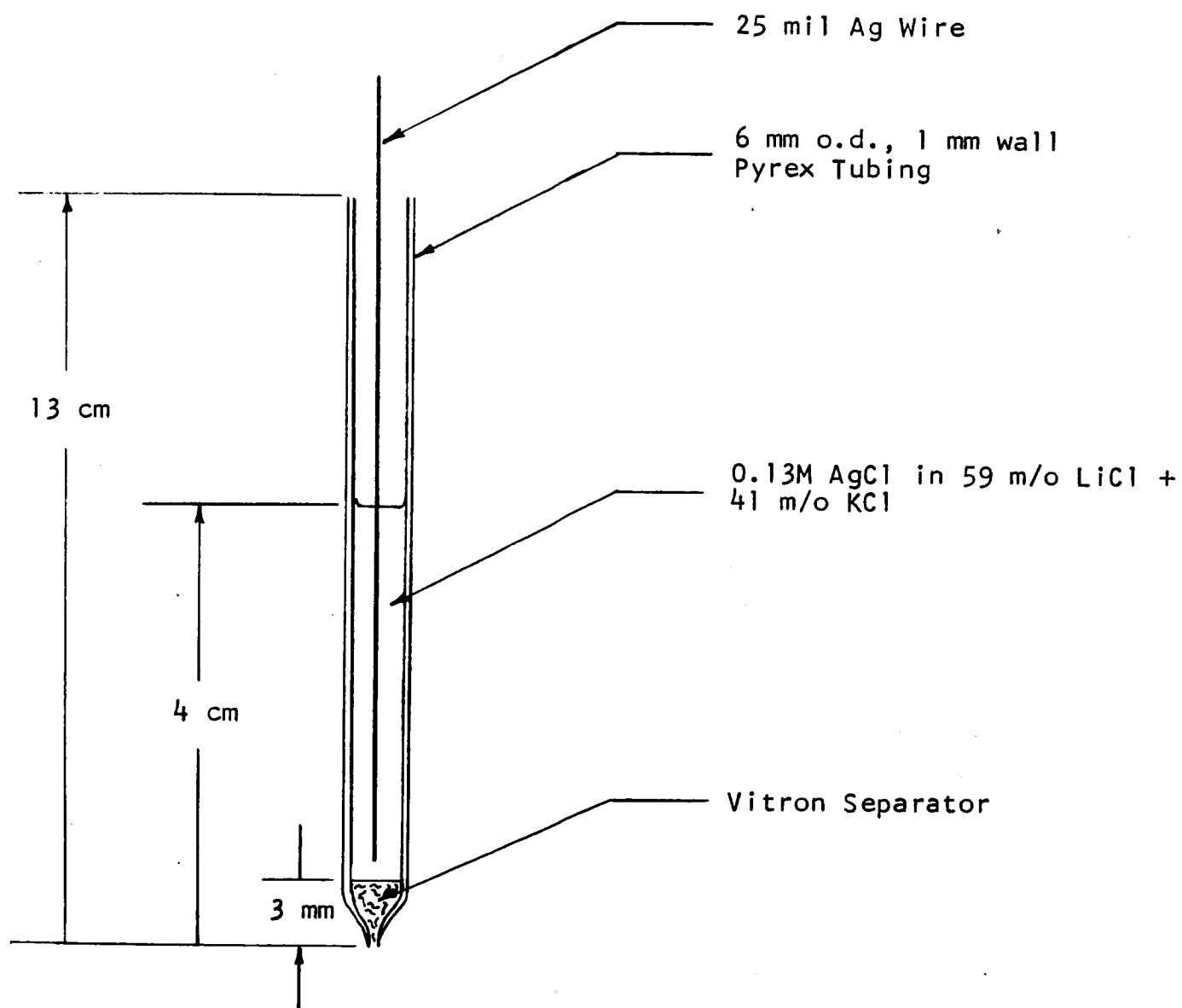
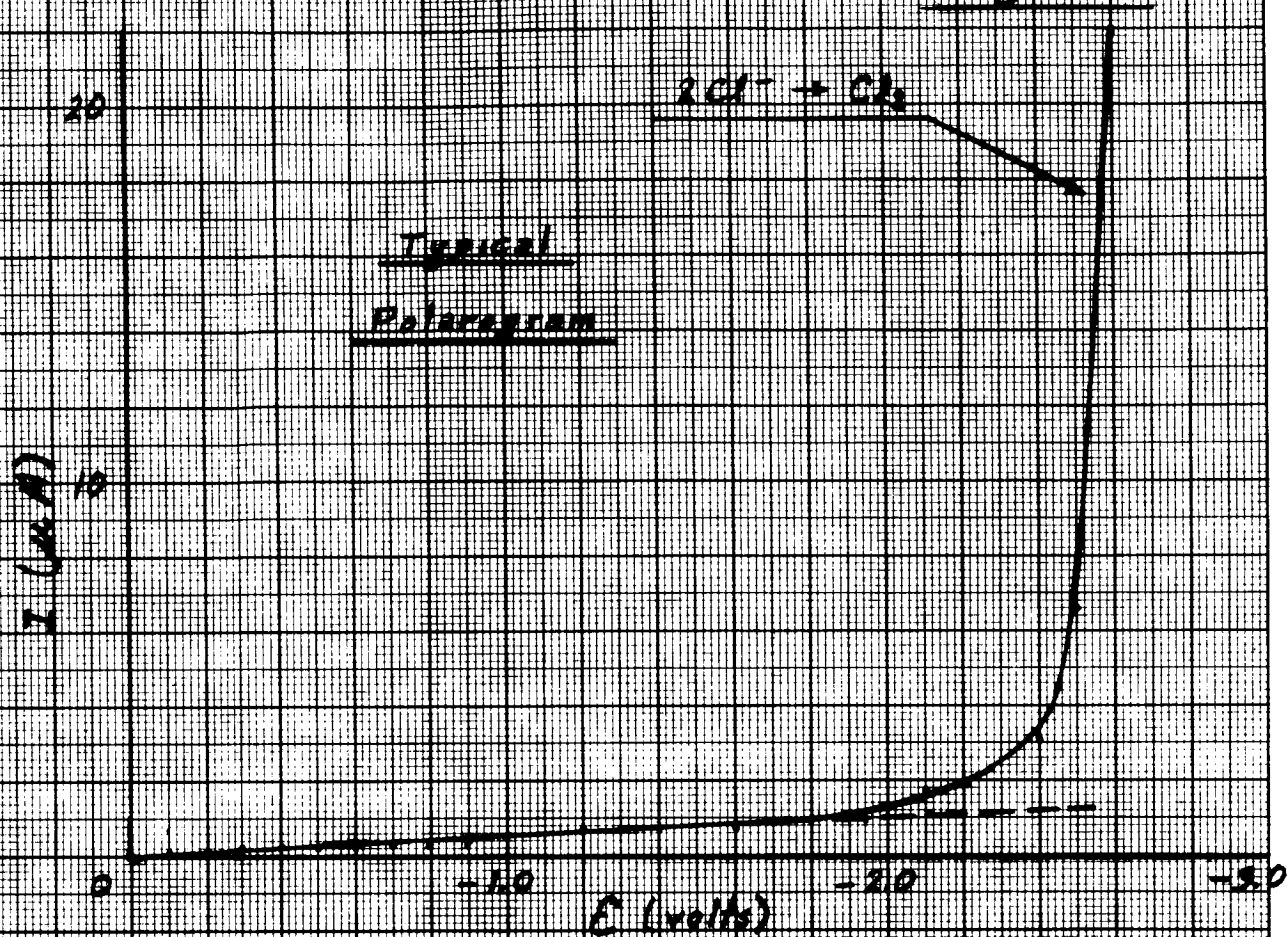


Fig. 8

Conditions:

50 Mole % LiCl + 50 Mole % KCl

Test Electrode ... 10 ml Pt wire

Counter Electrode	} 1 cm ² Pt foil
Reference Electrode	

Temperature ... 400°C

Figure 9

Ref. Electrode: $\text{Ag}/0.1\text{M AgCl}$
 Temp. $427 \pm 5^\circ\text{C}$

E vs. I Data

Pressed Powder Cathodes

100% CuO)

75% CuO)

50% CuO)

75% Cu_2O)

100% Cu_2O)

Pressed at 2
 50 tons/in.²

Pressed at 2
 400 lbs/in.²

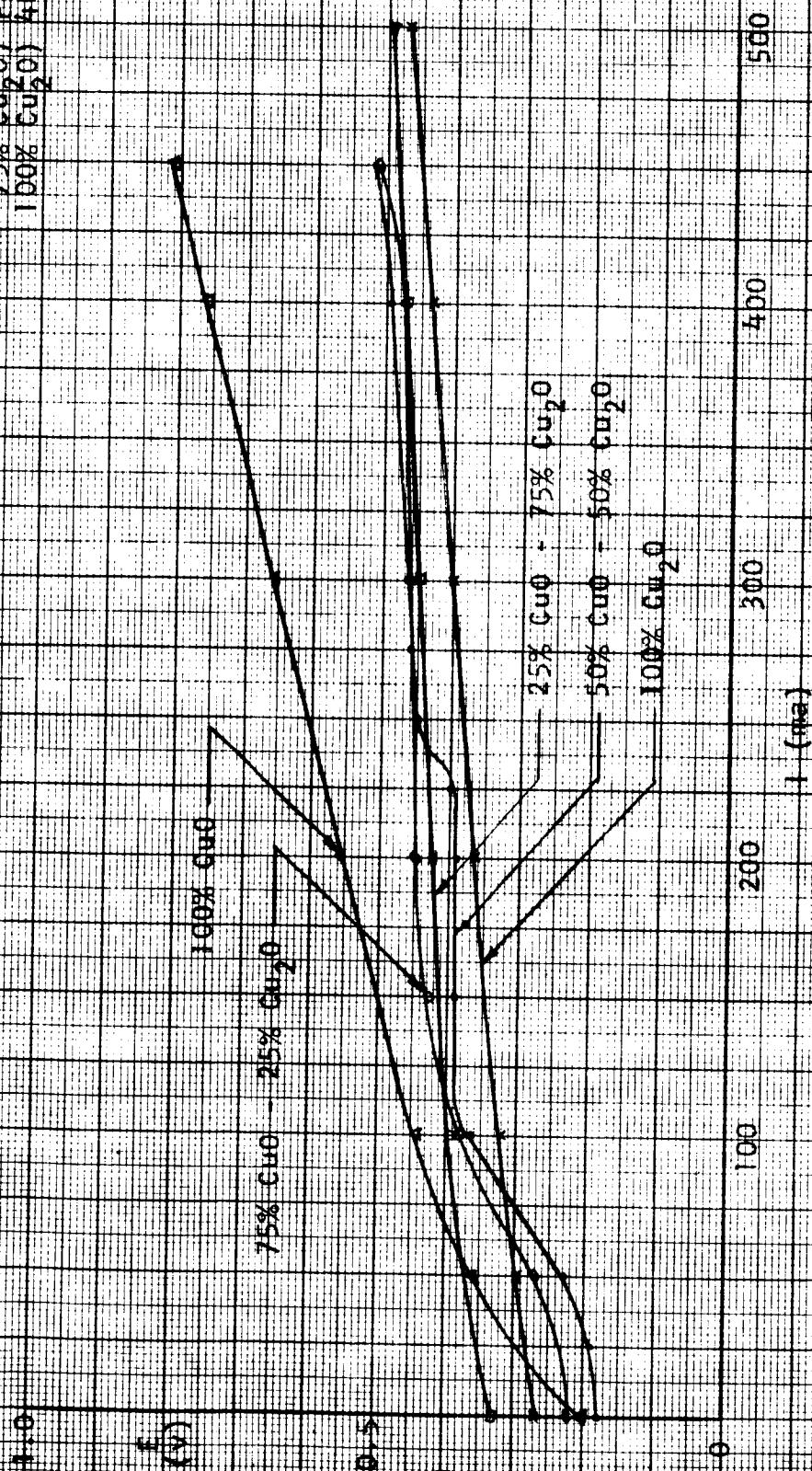


Figure 10

Ref. Electrode --- Ag/0.1M AgCl
Temp. --- 4.27 ± 5°C

E vs. I Data
Sintered Pressed Powder
Cathodes

100% CuO } Pressed at 2
75% CuO } 50 tons/in.
50% CuO }
75% Cu₂O } Pressed at 2
100% Cu₂O } 400 lbs/in.

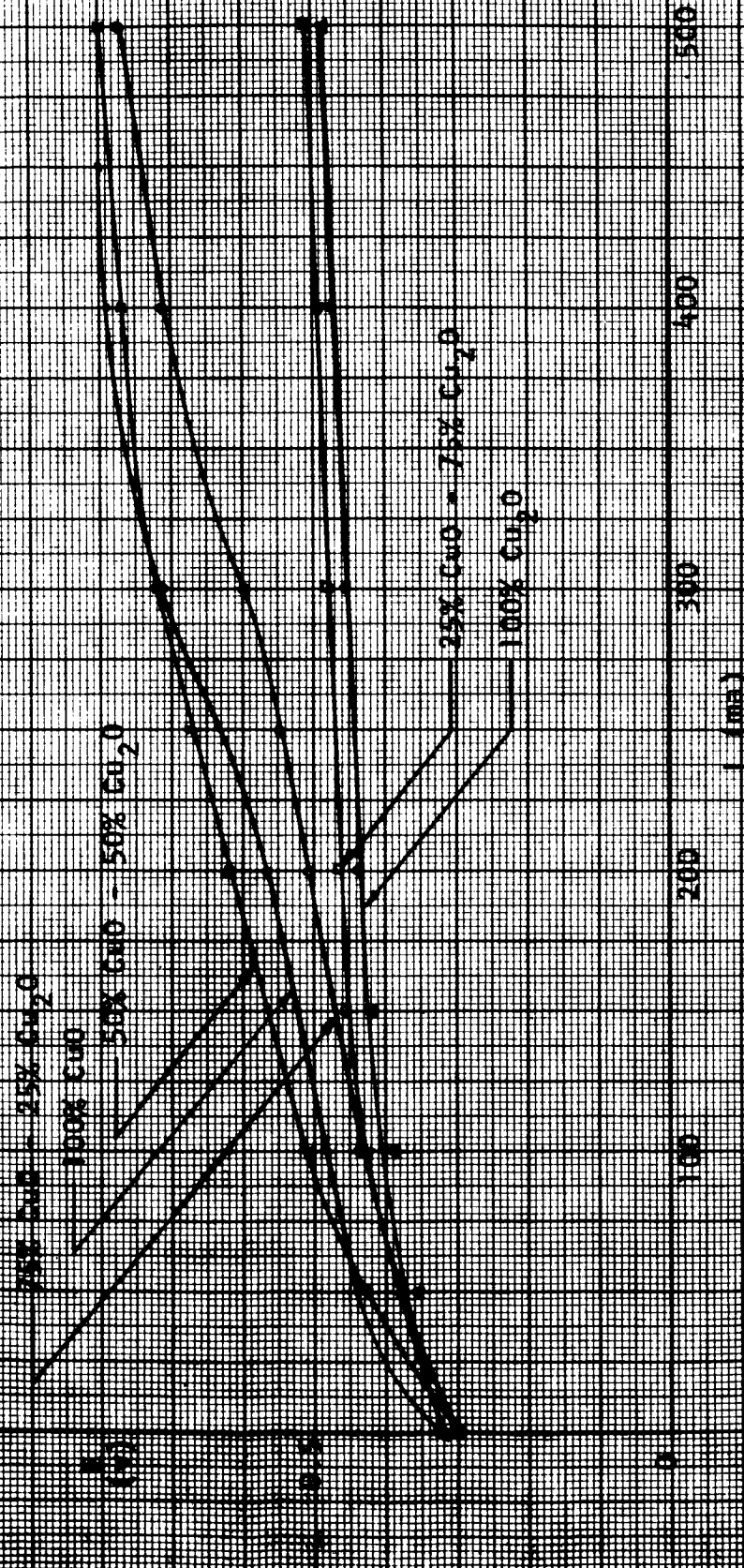
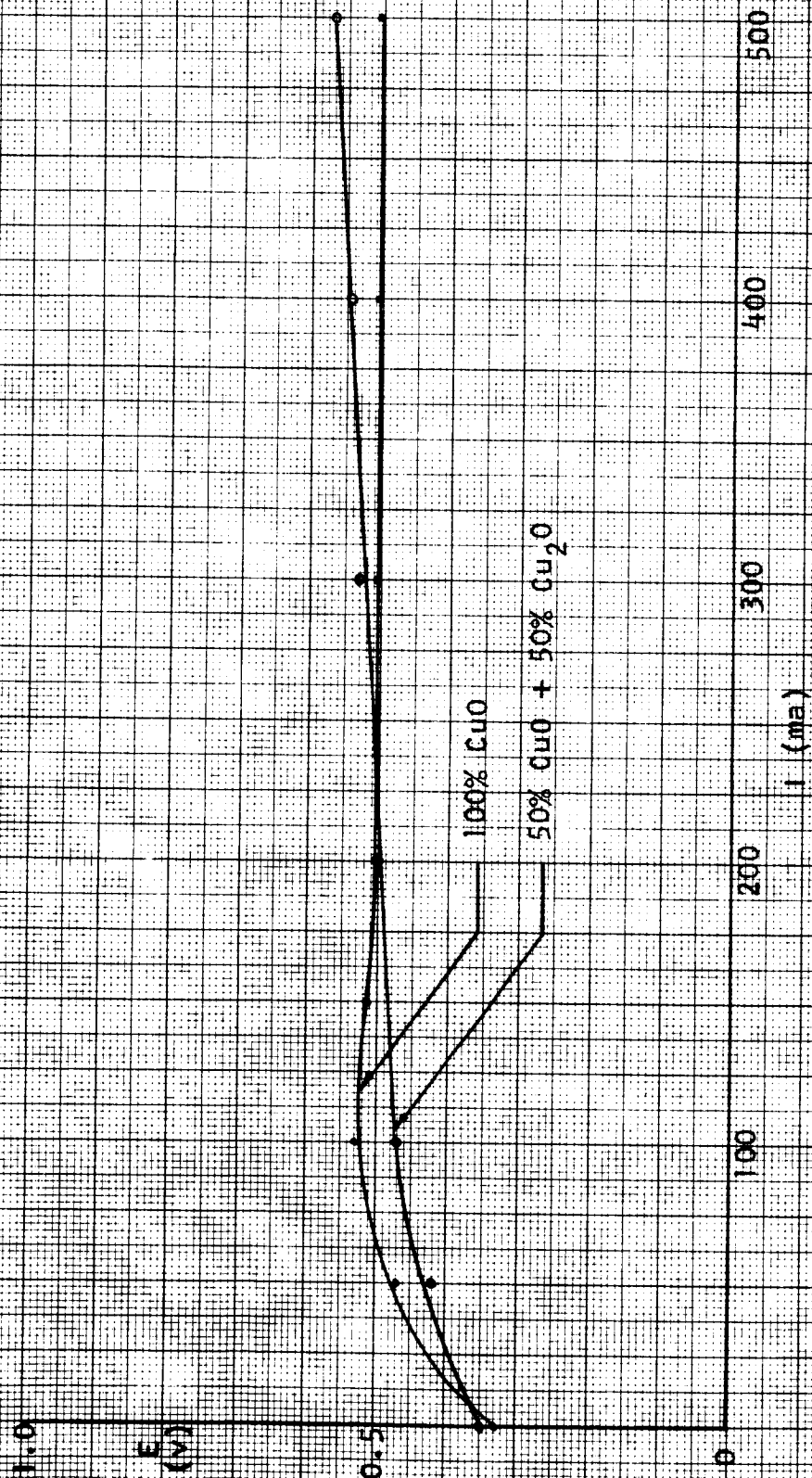


Figure 11

Ref. Electrode --- Ag/0.1M AgCl
Temp. --- 427 ± 5°C

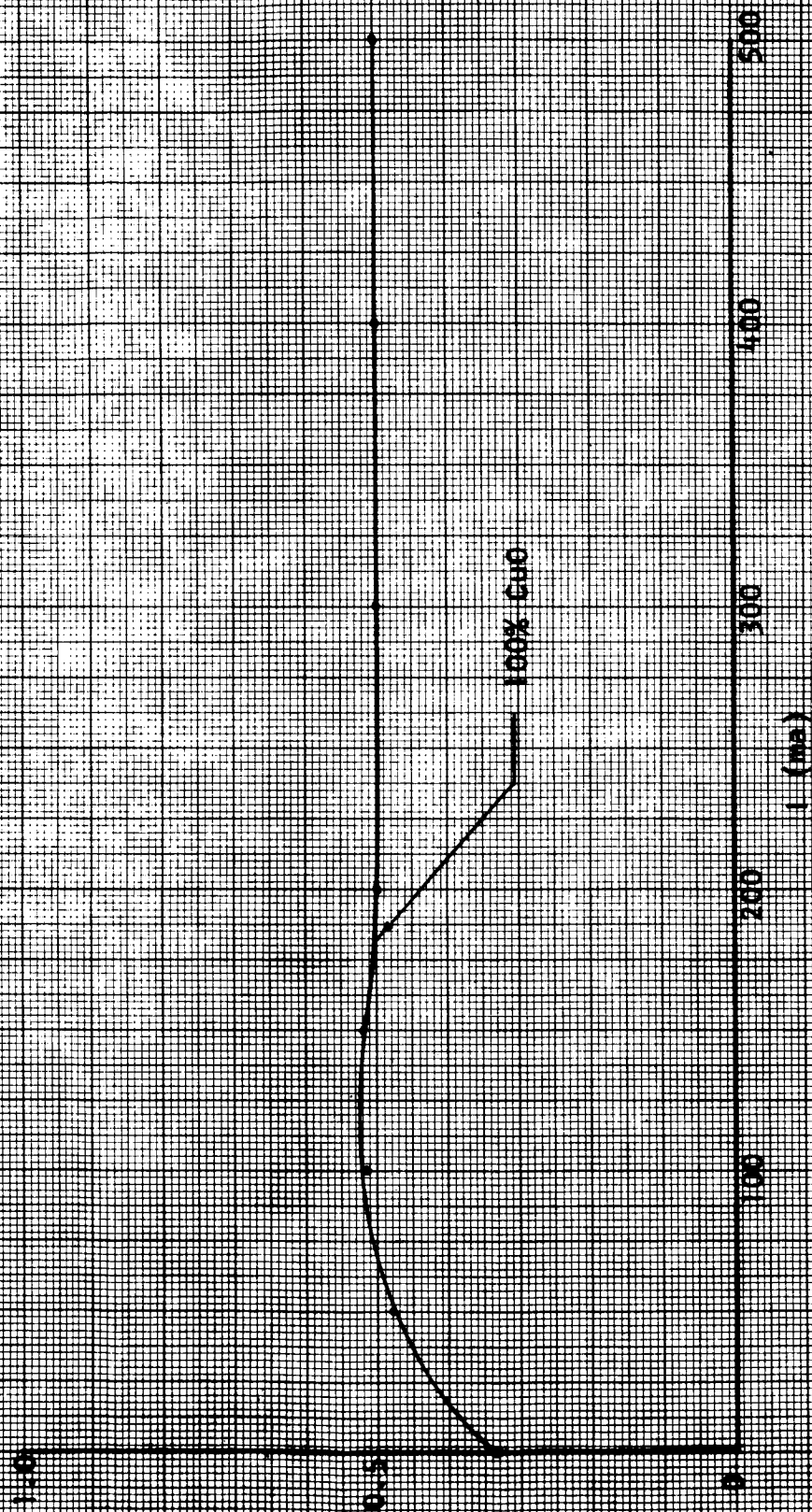
E vs. I Data
Copper Needle Cathodes
(6 mil Cu Needles)



E vs. I Data
Copper Grid Cathodes

Figure 12

Ref. Electrode --- Ag/0.13M AgCl
Temp. --- $427 \pm 5^\circ\text{C}$



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Figure 13

E vs. I Test Circuit

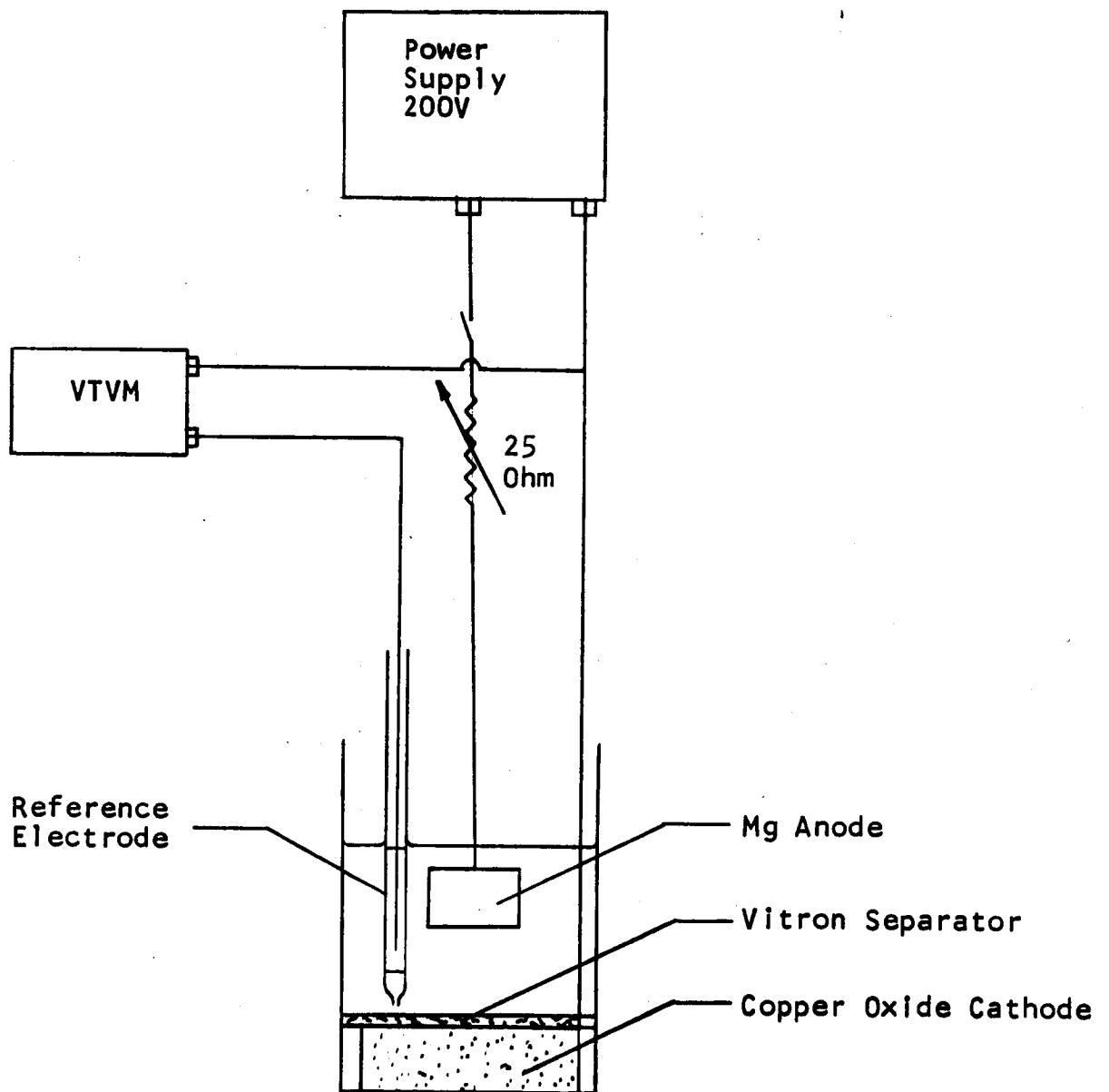
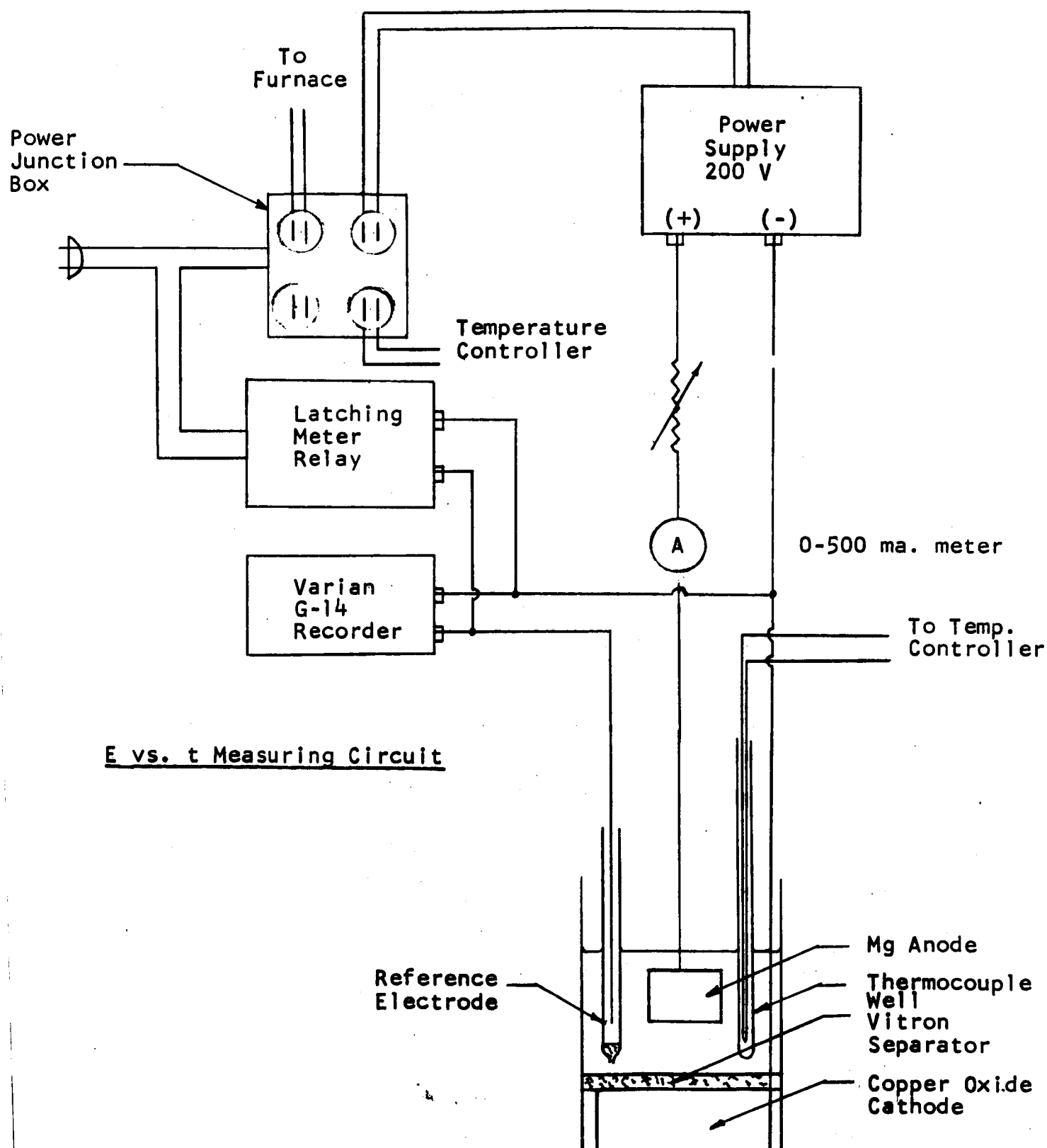


Figure 14



E vs. t Measuring Circuit

Figure 15

Ref. Electrode --- Ag/0.13M AgCl
 Temp. --- 427 ± 5°C; I = 264 ma

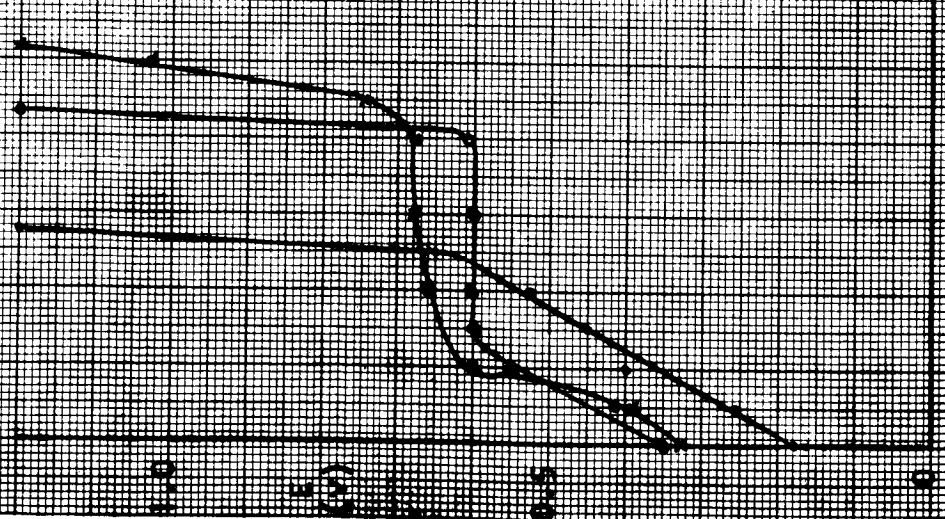
E vs. t Data
 2-Day Tests
 Pressed Powder Cathodes
 100% Cu₂O

Test Number

11

1

1



Time (Mins)

E vs. t Date
2-Day Tests
Pressed Powder
75% CuO + 25%

Figure 16

Ref. electrode --- Ag/0.1M AgC
Temp. --- 427 ± 5°C; --- 264 ma

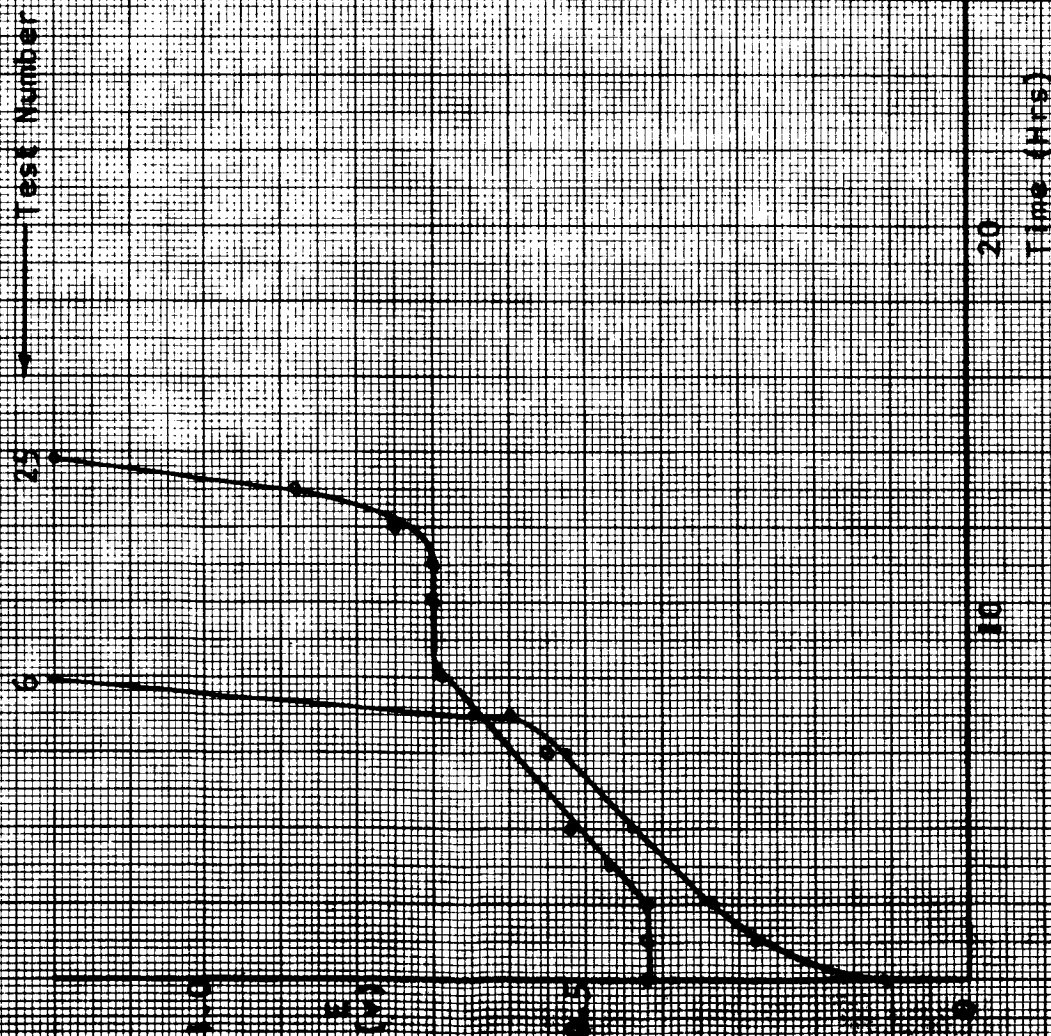


Figure 17

Ref. Electrode --- Ag/0.13M AgCl
Temp. --- 42.7 ± 5°C; I = 264 ma

E vs. t Data
2-Day Tests
Pressed Powder Cathode
50% CuO + 50% Cu₂O

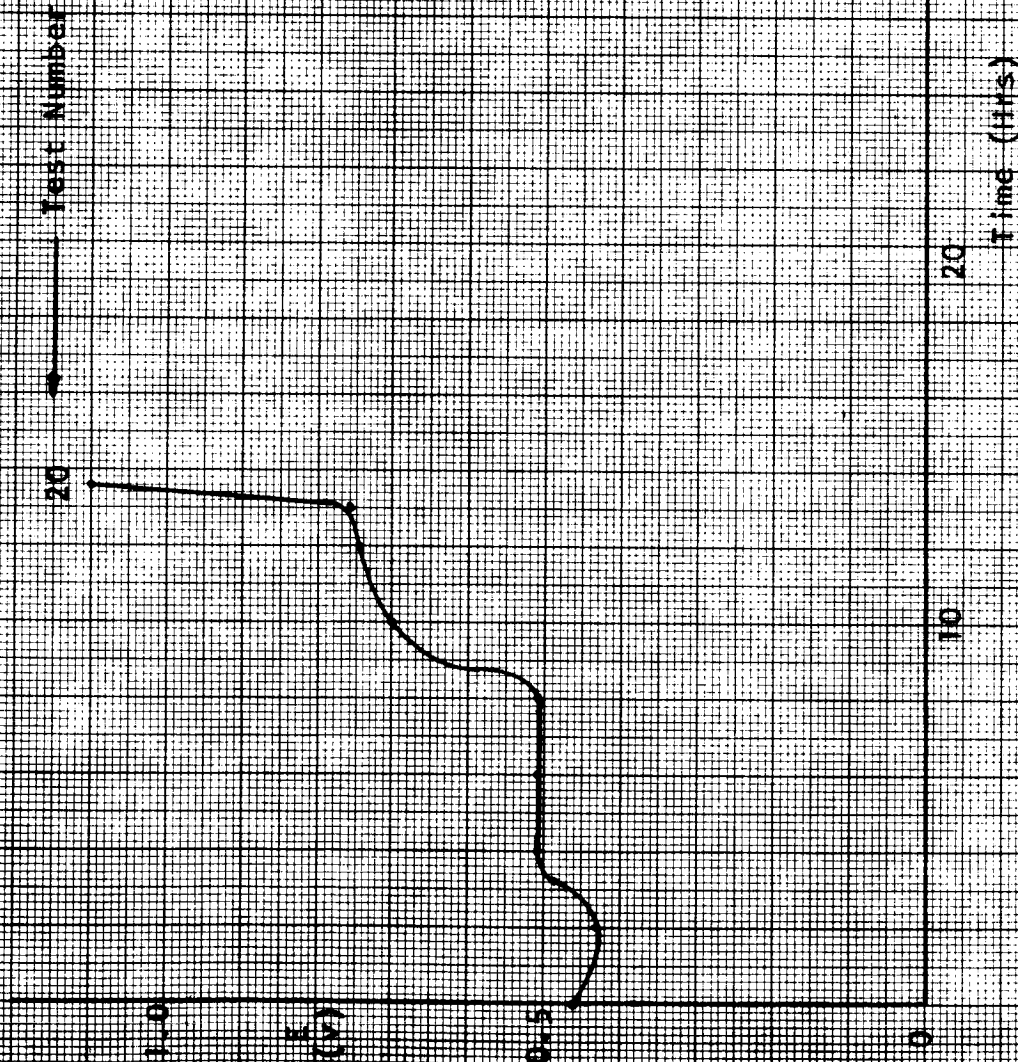


Figure 18

Ref. Electrode --- Ag/0.13N AgCl
 Temp. --- $42.7 \pm 5^\circ\text{C}$ --- 264 ma

E vs. t Data
 2-Day Tests
 pressed powder Cathode
 25% CuO + 75% Cu₂O

Test Number --- 22

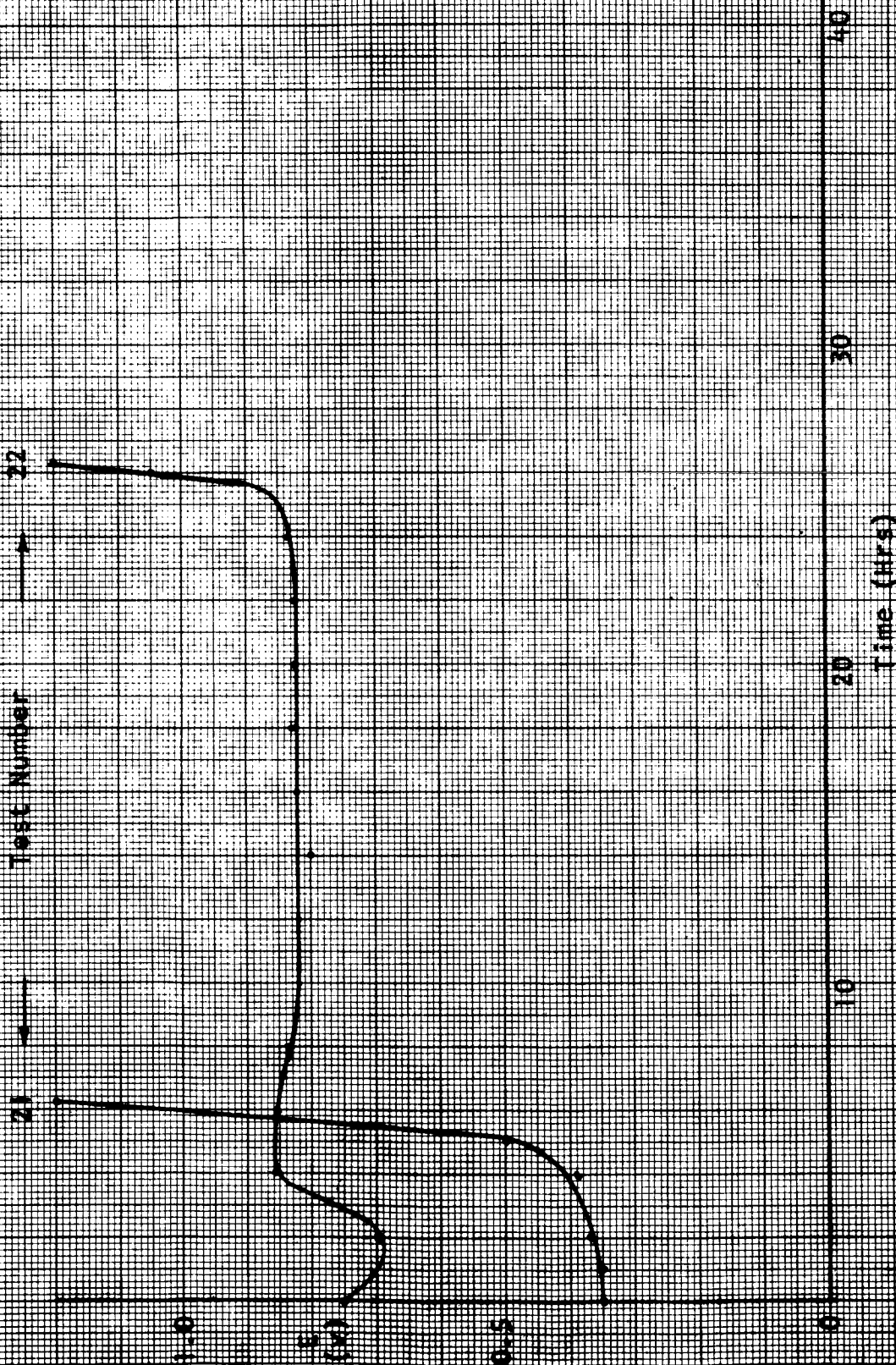


Figure 19

E vs. t Data
2-Day Tests
Pressed Powder Cathodes
100% Cu_2O

Ref. Electrode --- Ag/0.1M AgCl
Temp. --- $42.7 \pm 5^\circ\text{C}$; $i = 264 \text{ ma}$

Test Number

24

1.0

E (v)

0.5

0

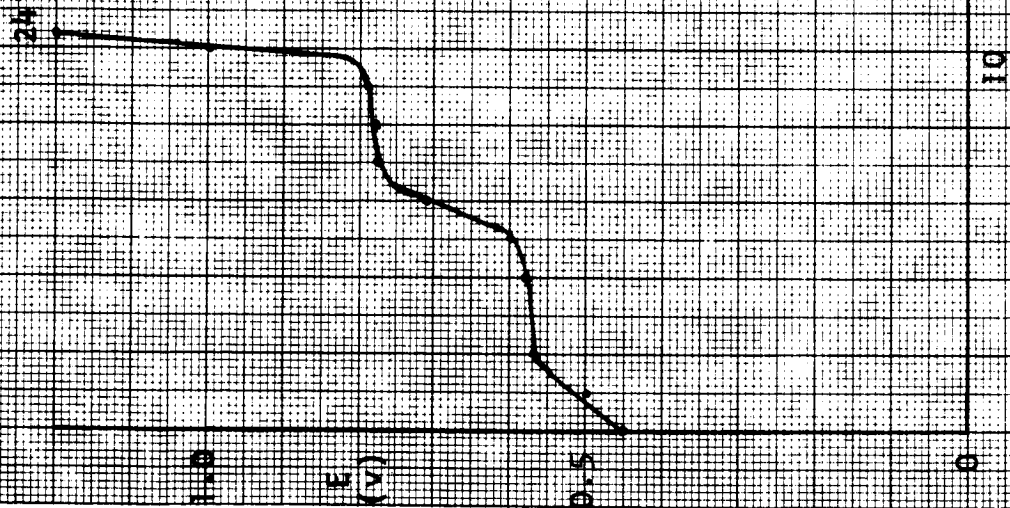
10

20

30

40

Time (Hrs)



E vs. t Data
6-Day Tests
Pressed Powder Cathodes
100% CuO

Figure 20
Ref. Electrode -- Ag/0.1M AgCl
Temp. -- 427 ± 5°C, I = 87.5 ma

Test Number

44

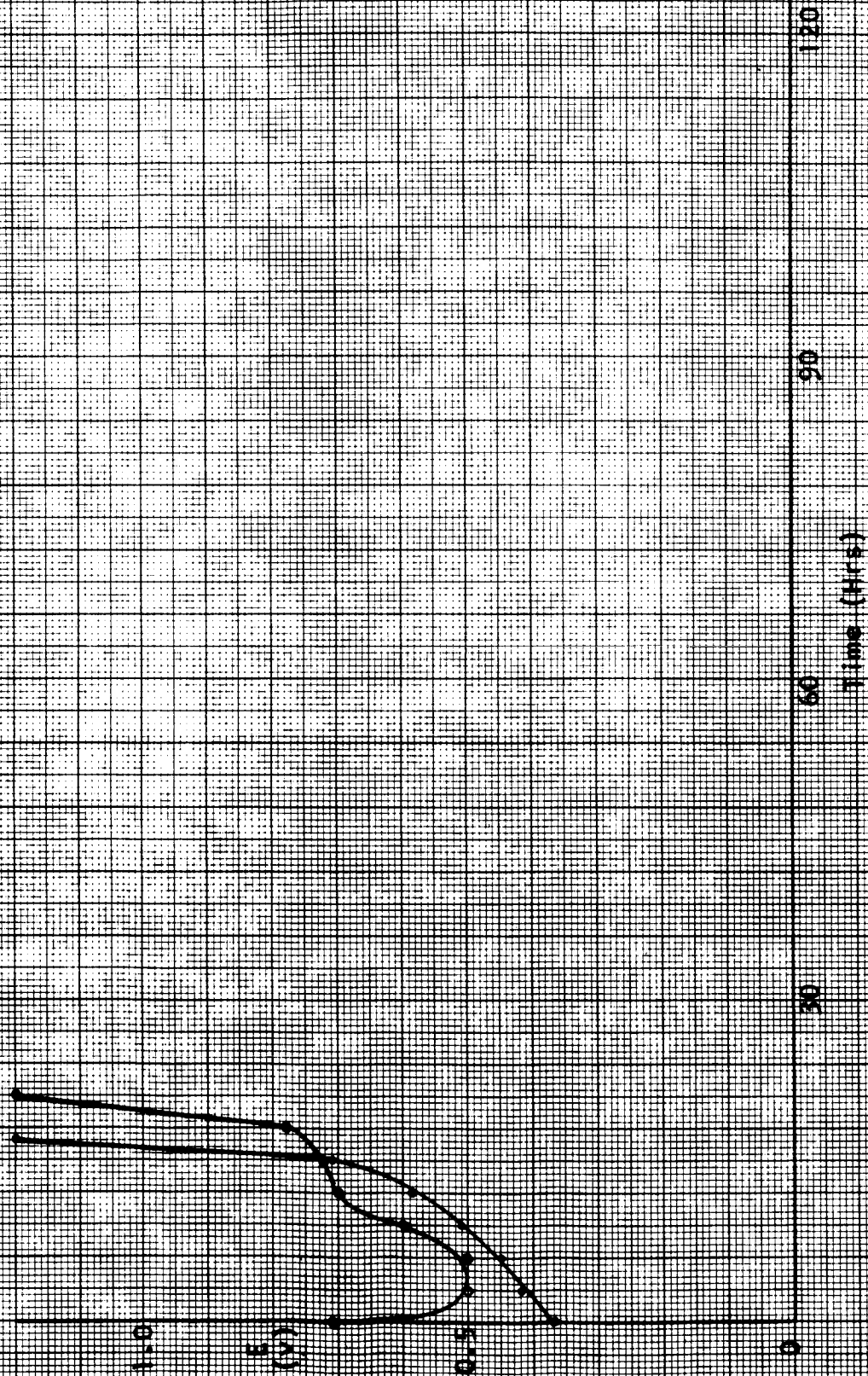


Figure 2

Ref. Electrode --- Ag/0.1M AgCl
Temp. --- 42.7 ± 5°C. --- 87.5 ma

E vs. t Data
6-Day Tests
Pressed Powder Cathodes
75% CuO + 25% Cu₂O

Test Number

45

1.0

E (V)

0.5

0

30

60

90

120

Time (Hrs.)



Figure 22

Ref. Electrode: Ag/AgCl 0.1M AgCl
Temp.: $22 \pm 5^\circ\text{C}$ $\pm 87.5 \text{ mV}$

Test Number: 43

43

E vs. t Data
6-Day Tests
pressed Powder Cathode
50% CuO + 50% Cu_2O

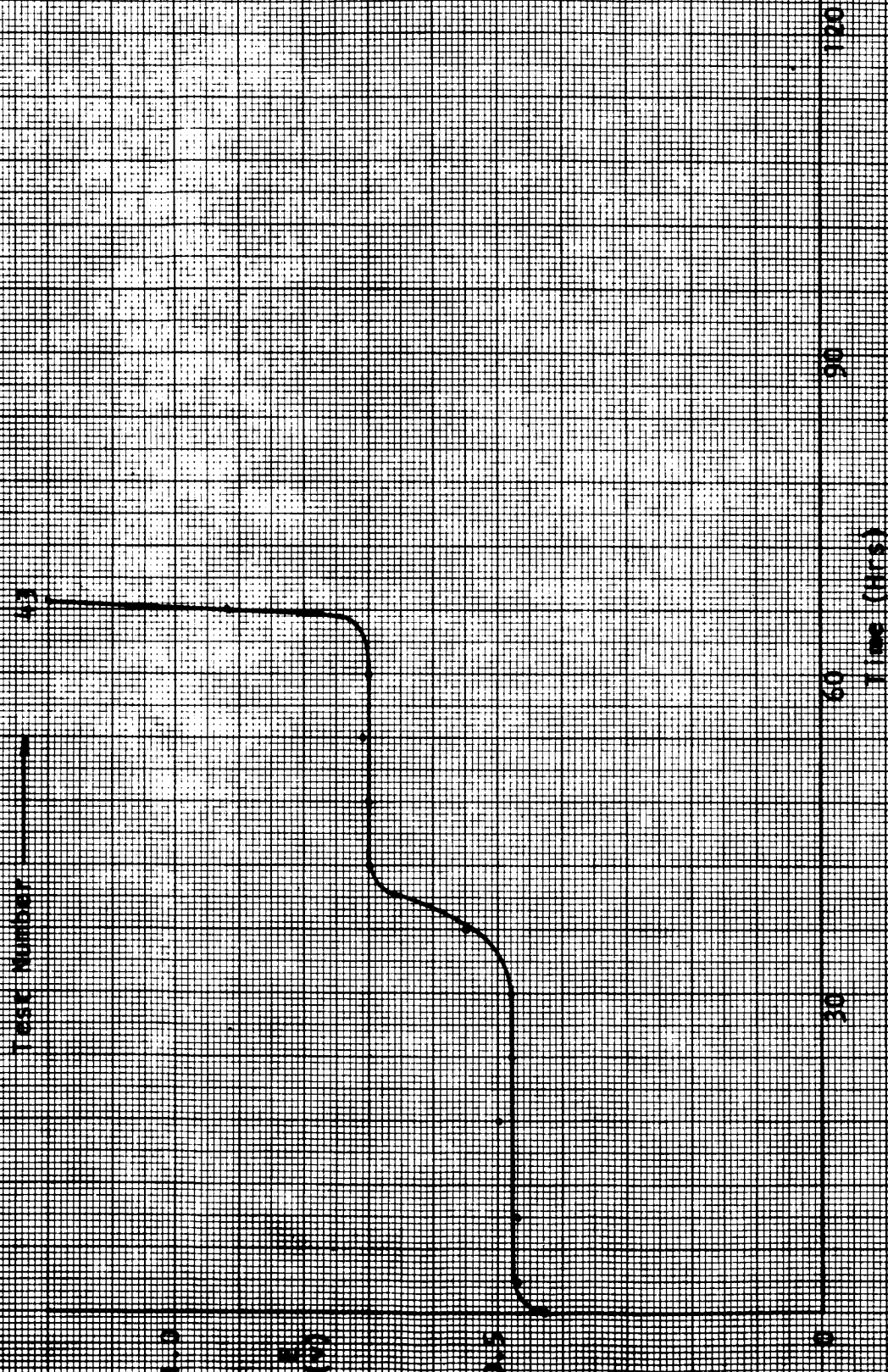


Figure 23

Ref. Electrode --- Ag/0.1M AgCl
Temp. --- $42.7 \pm 5^\circ\text{C}$ --- 87.5 ma

E vs. t Data
6-Day Test
Pressed Powder Cathode
75% Cu_2O + 25% CuO

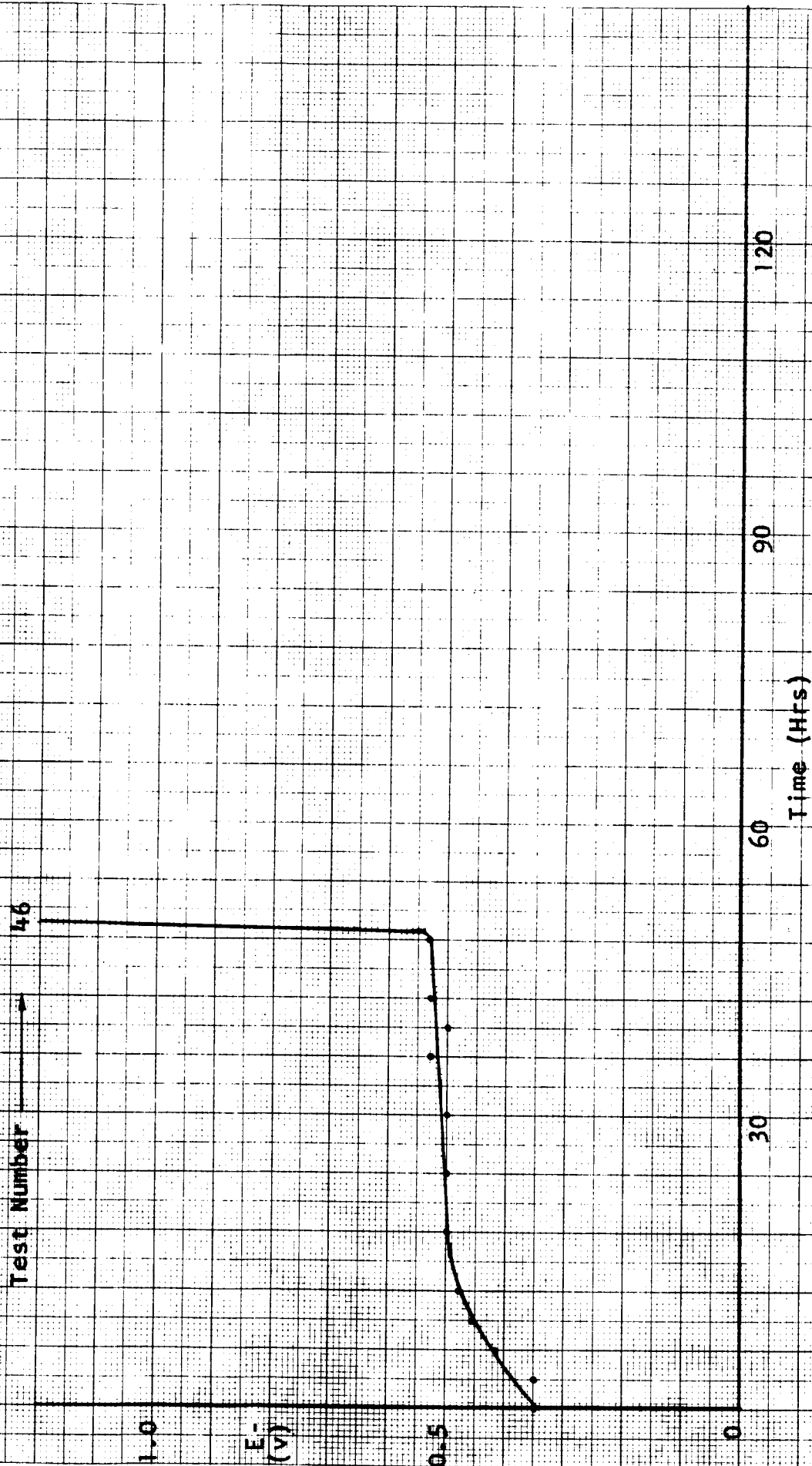


Figure 24

Ref. Electrode --- Ag/0.1M AgCl
Temp. --- $427 \pm 5^\circ\text{C}$; $i = 87.5 \text{ ma}$

E vs. t Data
6-Day Test
Pressed Powder Cathodes
100% Cu_2O

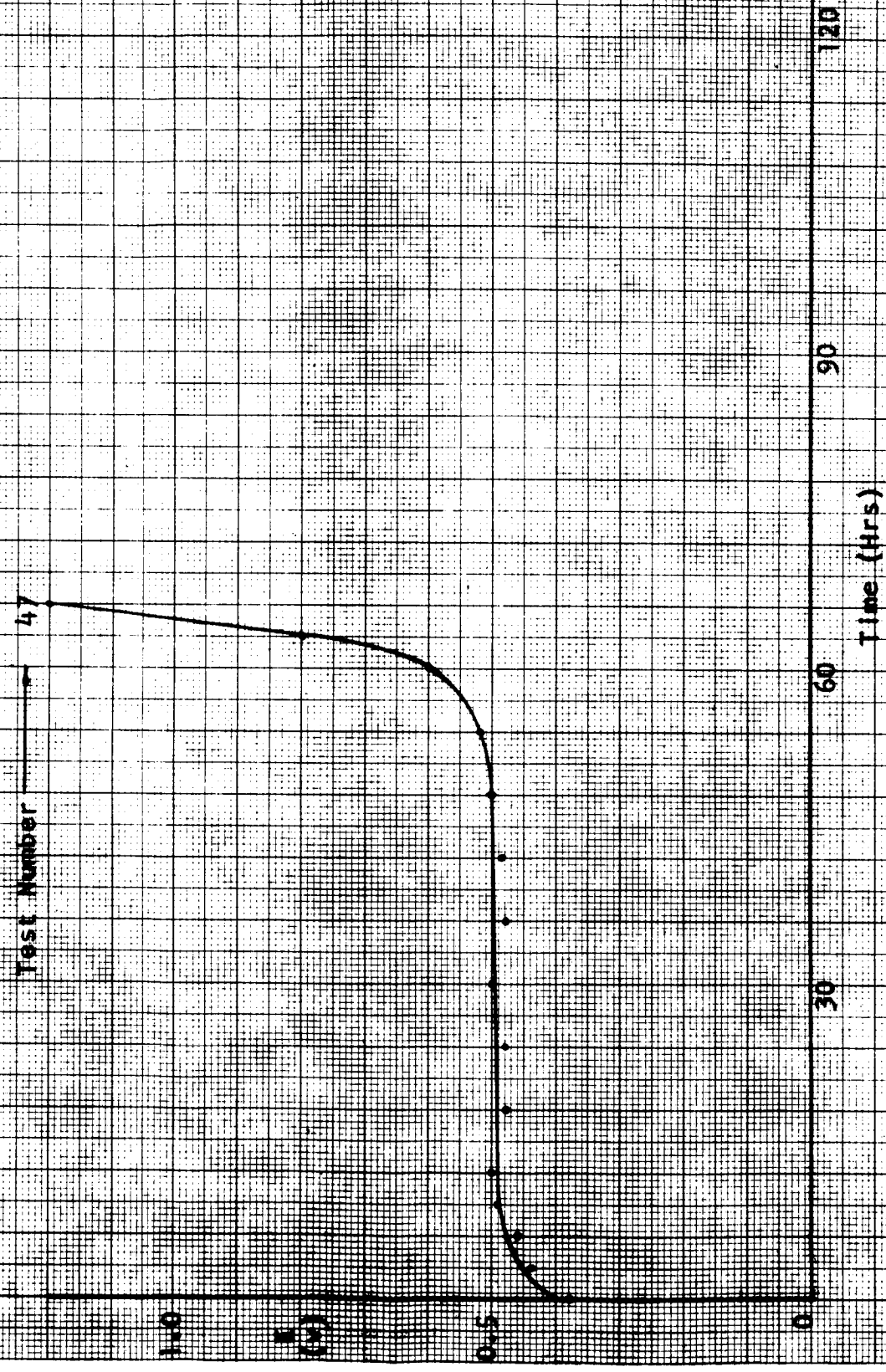


Figure 25

Ref. Electrode --- Ag/0.13M AgCl
Temp. --- 427 ± 5°C; I = 264 ma

E vs. t Data
2-Day Tests
Sintered Pressed Powder
Cathodes
100% CuO

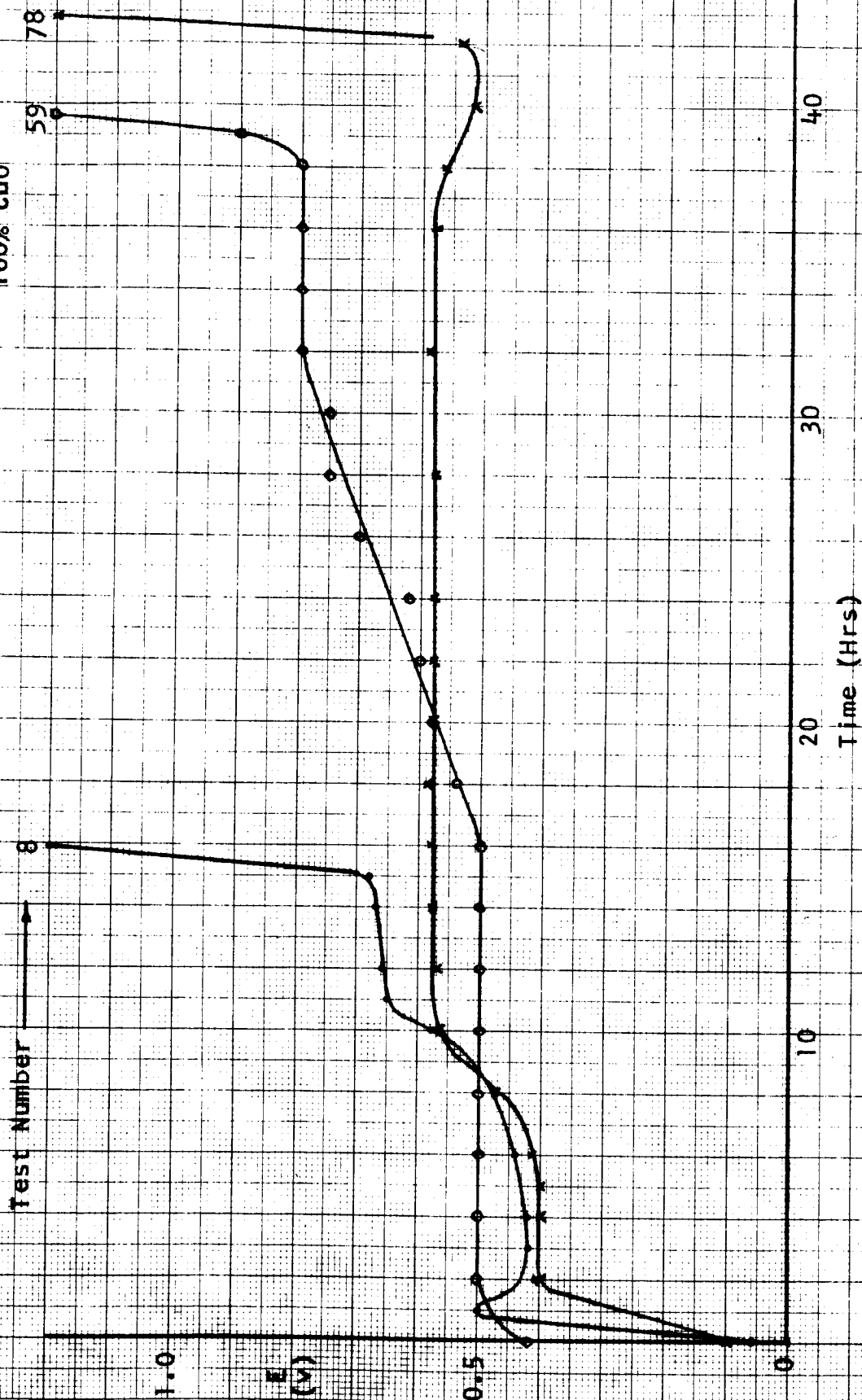


Figure 26

Ref. Electrode --- Ag/0.13M AgCl
Temp. --- $427 \pm 5^{\circ}\text{C}$; $I = 264 \text{ ma}$

E vs. t Data
2-Day Test

Sintered Pressed Powder
Cathode
 $75\% \text{ CuO} + 25\% \text{ Cu}_2\text{O}$

Test Number → 29

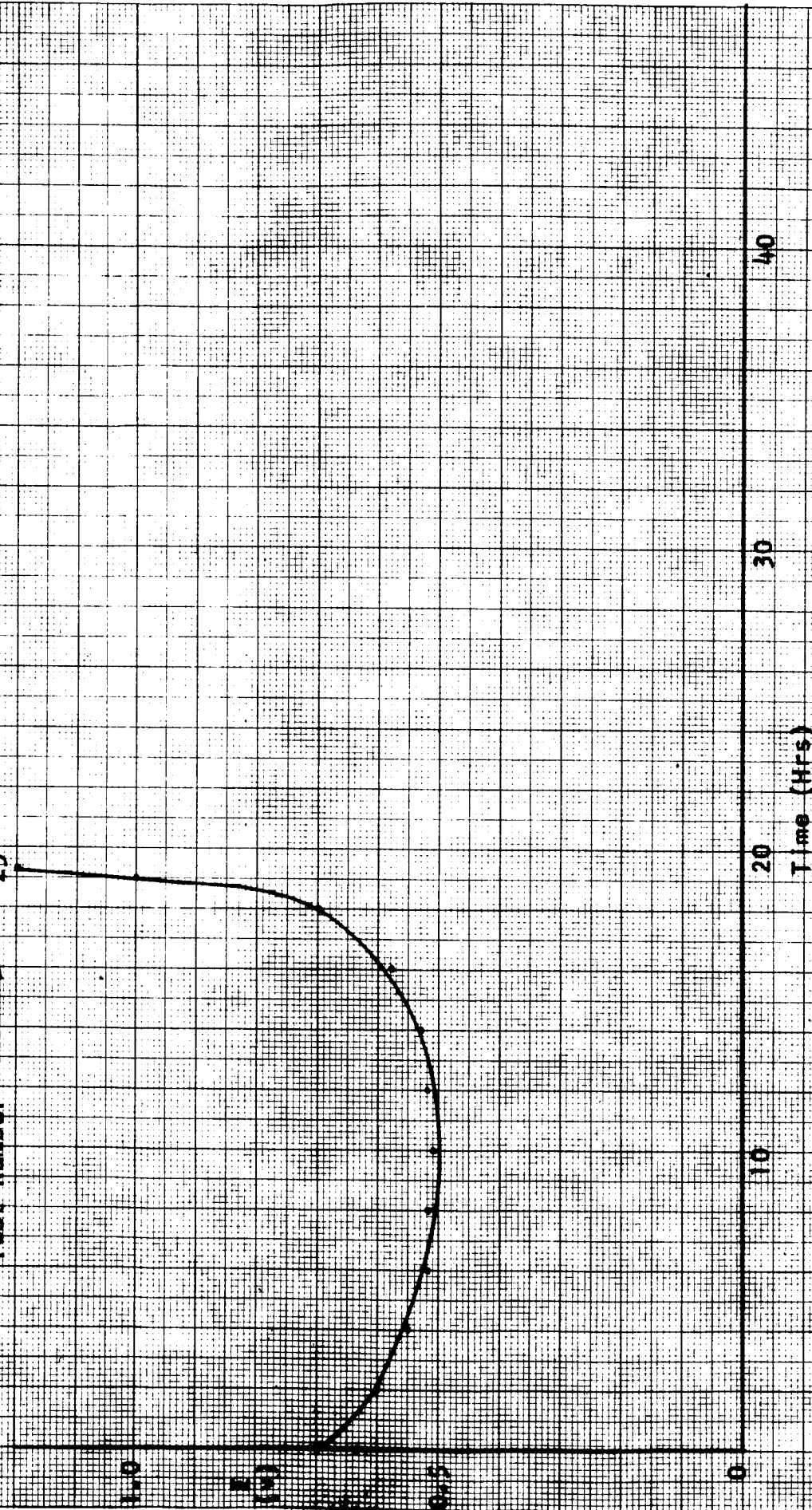


Figure 27

Ref. Electrode -- Ag/0.1M AgCl
Temp. -- $42.7 \pm 5^\circ\text{C}$, $I = 264\text{ mA}$

E vs. t Data
2-Day Test
Sintered Pressed Powder
Cathode
 $50\% \text{ CuO} + 50\% \text{ Cu}_2\text{O}$

Test Number 27

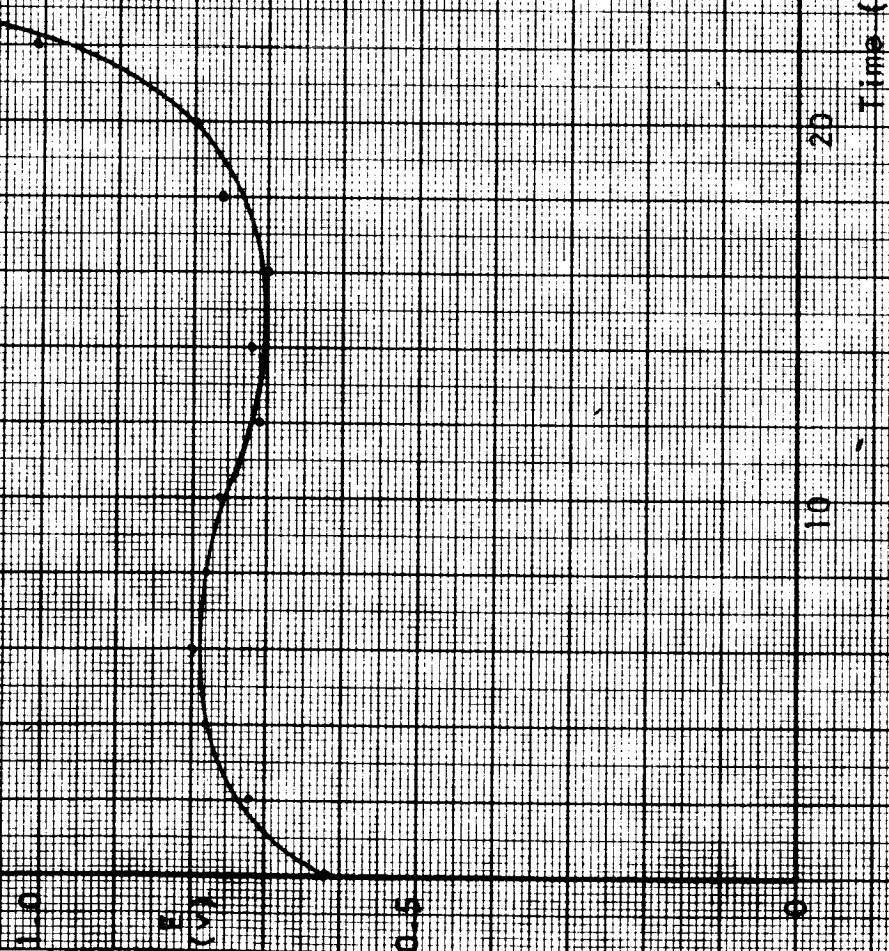


Figure 28

Ref. Electrode --- Ag/0.1M AgCl
 Temp. --- 427 ± 5°C
 Cathode --- 25% CuO + 75% Cu₂O

E vs. t Data
 2-Day Tests
 Sintered Pressed Powder
 Cathodes
 25% CuO + 75% Cu₂O



Figure 29

Ref. Electrode --- Ag/0.13M AgCl
Temp. --- $42.7 \pm 5.0^\circ\text{C}$; $\rightarrow 264\text{ mls}$

E vs. t Data
2-Day Tests
Sintered pressed powder
Cathodes
100% Cu₂O

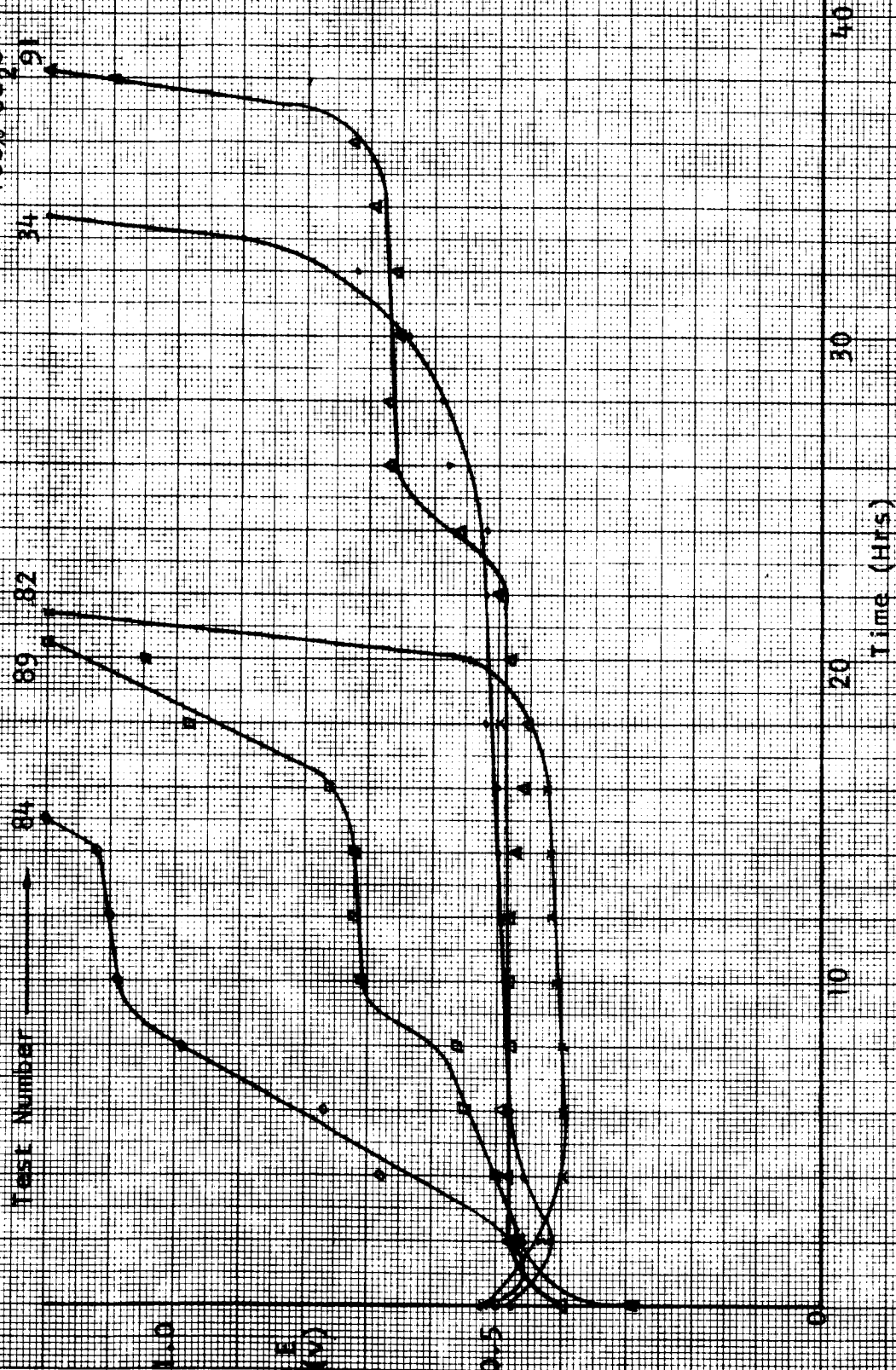


Figure 30

Ref. Electrode -- Ag/0.1M AgCl
Temp. -- 427 ± 5°C -- 87.5 ma

E vs. τ Data
6-Day Tests
Sintered Pressed powder
Cathodes
100% CuO

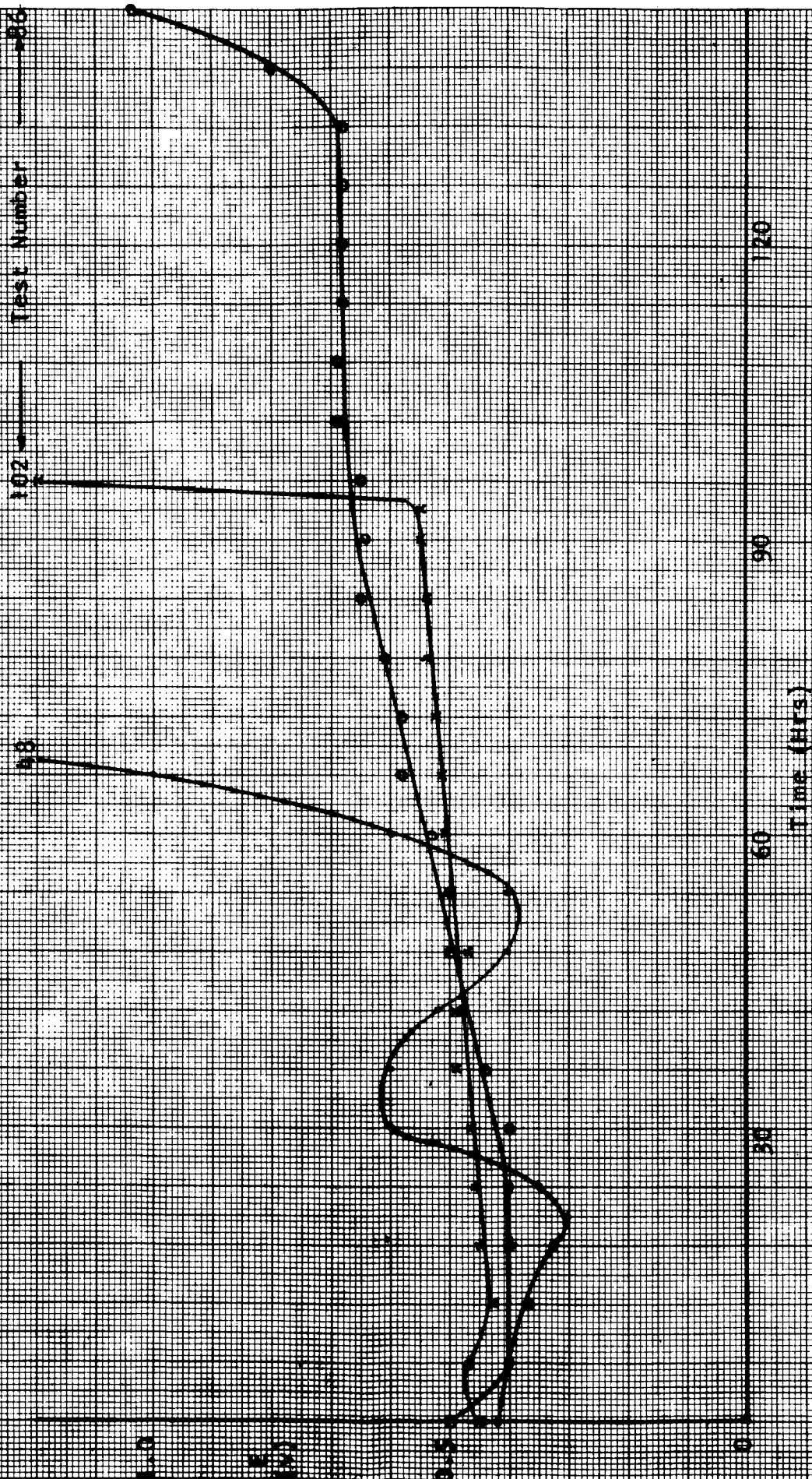


Figure 31

Ref. Electrode --- Ag/0.1M AgCl
Temp. --- 42.7 ± 5°C | 87.5 ma

E vs. t Data

6-Day Test
Sintered pressed Powder
Cathodes
75% CuO + 25% Cu₂O

Test Number 49

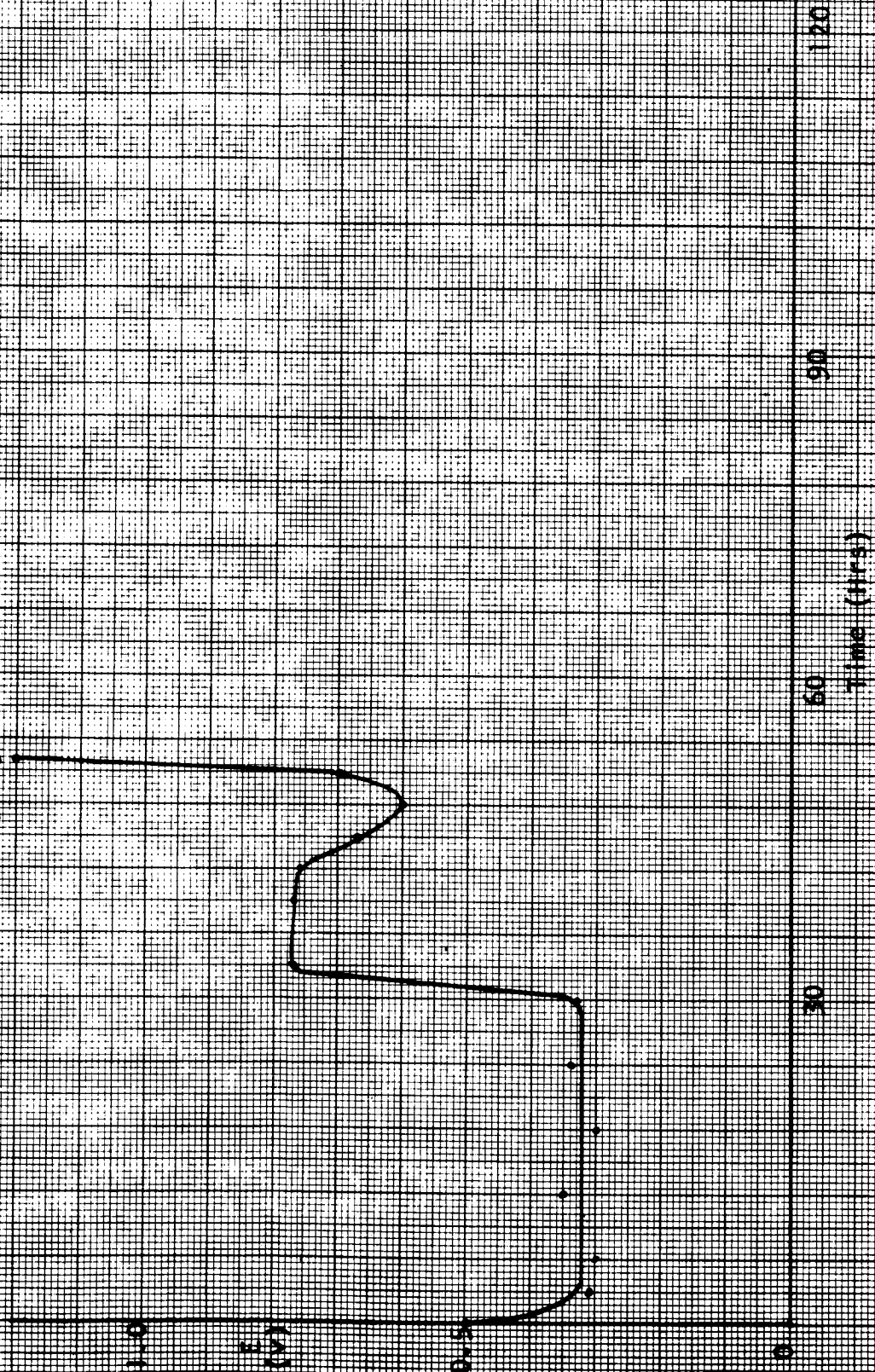


Figure 32

Ref. Electrode --- Ag/0.13M AgCl
Temp. --- 427 ± 5°C; i = 87.5 ma

E vs. t Data

6-Day Tests
Sintered Pressed Powder
Cathodes

25% CuO + 75% Cu₂O
79 251

Test Number --- 97

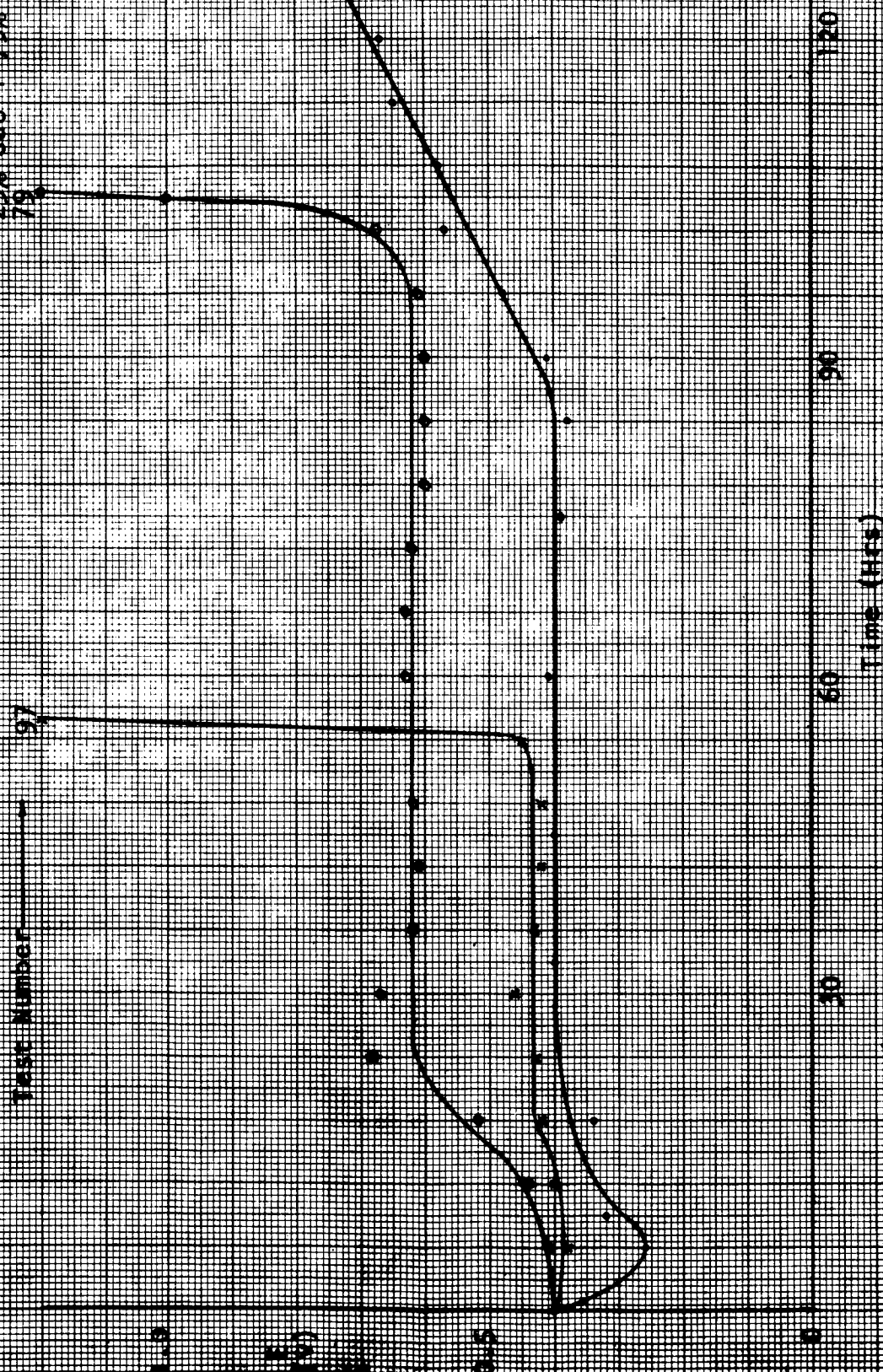


Figure 33

Ref. Electrode --- Ag/0.13M AgCl
 Temp. --- 427 ± 5°C; I = 87.5 ma

E vs. t Data
 6-Day Tests
 Sintered Pressed Powder
 Cathodes
 100% Cu₂O

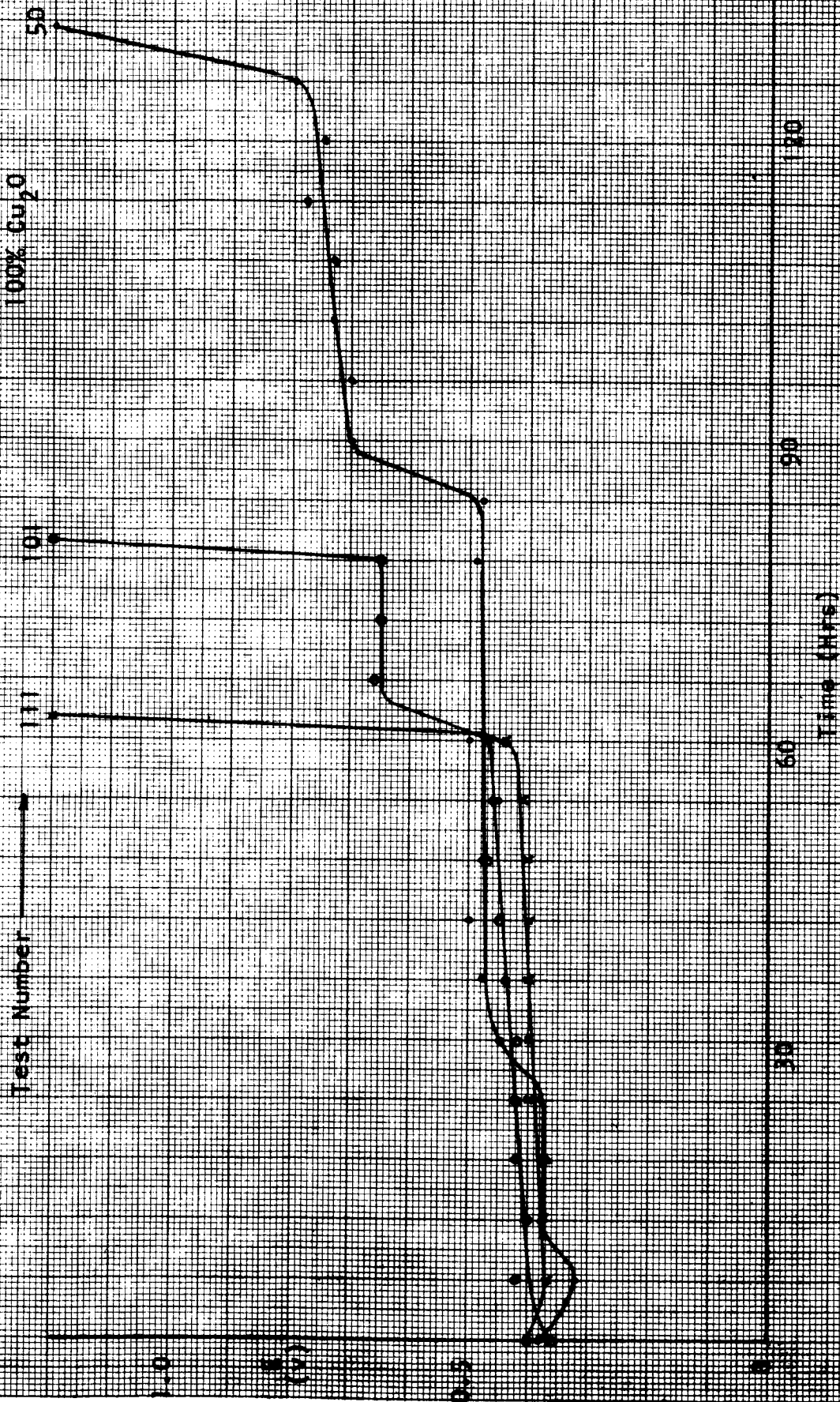


Figure 34

Ref. Electrode -- Ag/0.1M AgCl
Temp. -- 42.7 ± 5°C. → 264 ma

E vs. c Data
2-day Tests
Copper Needle Cathodes
(0.005 Cu)

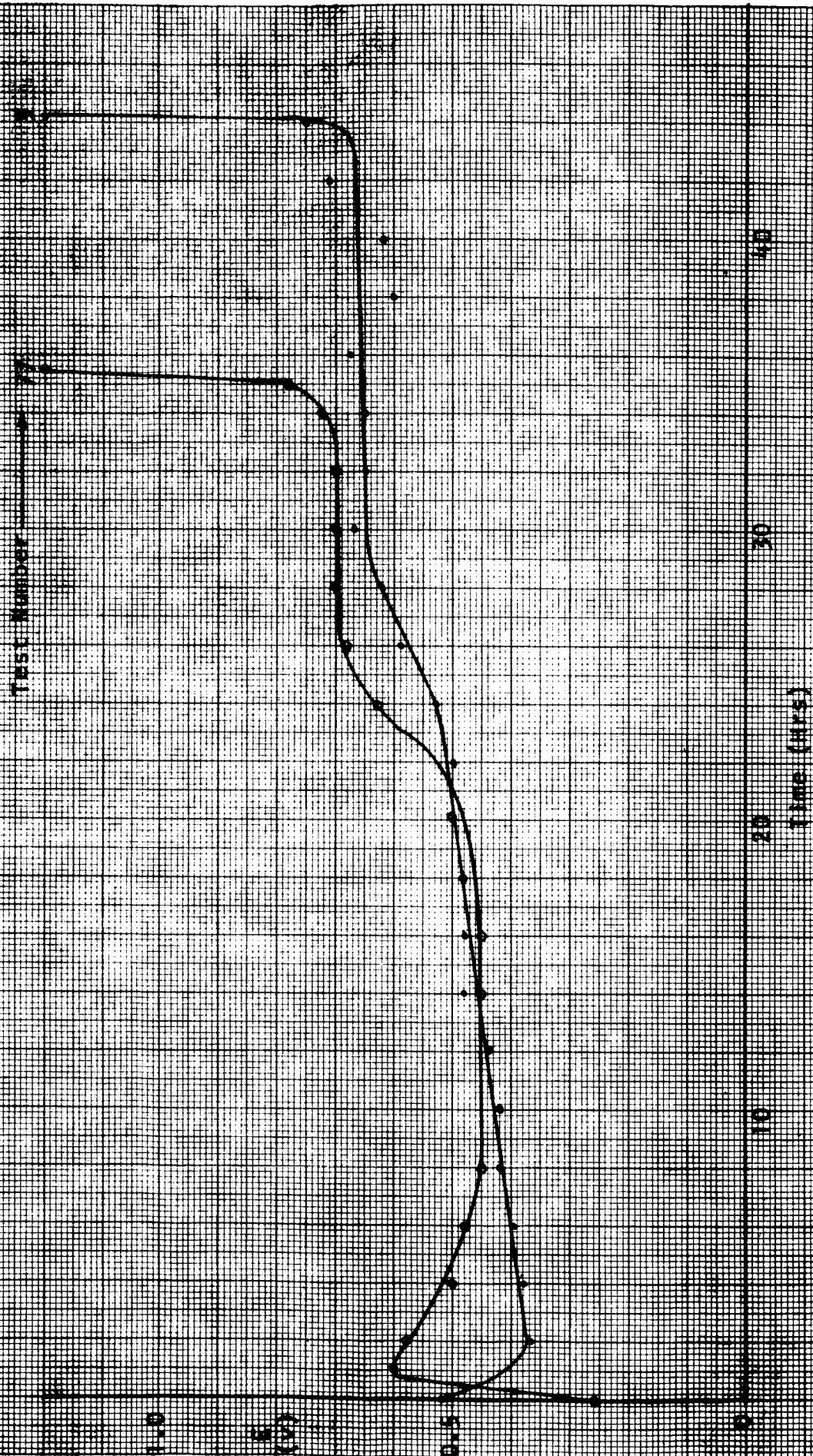


Figure 35

Ref. Electrode --- Ag/0.1M AgCl
Temp. --- 427 ± 5°C; $t = 264$ ms

E vs. t Data

2-Day Test

Copper Needle Cathode
75% CuO + 25% Cu₂O

Test Number --- 23

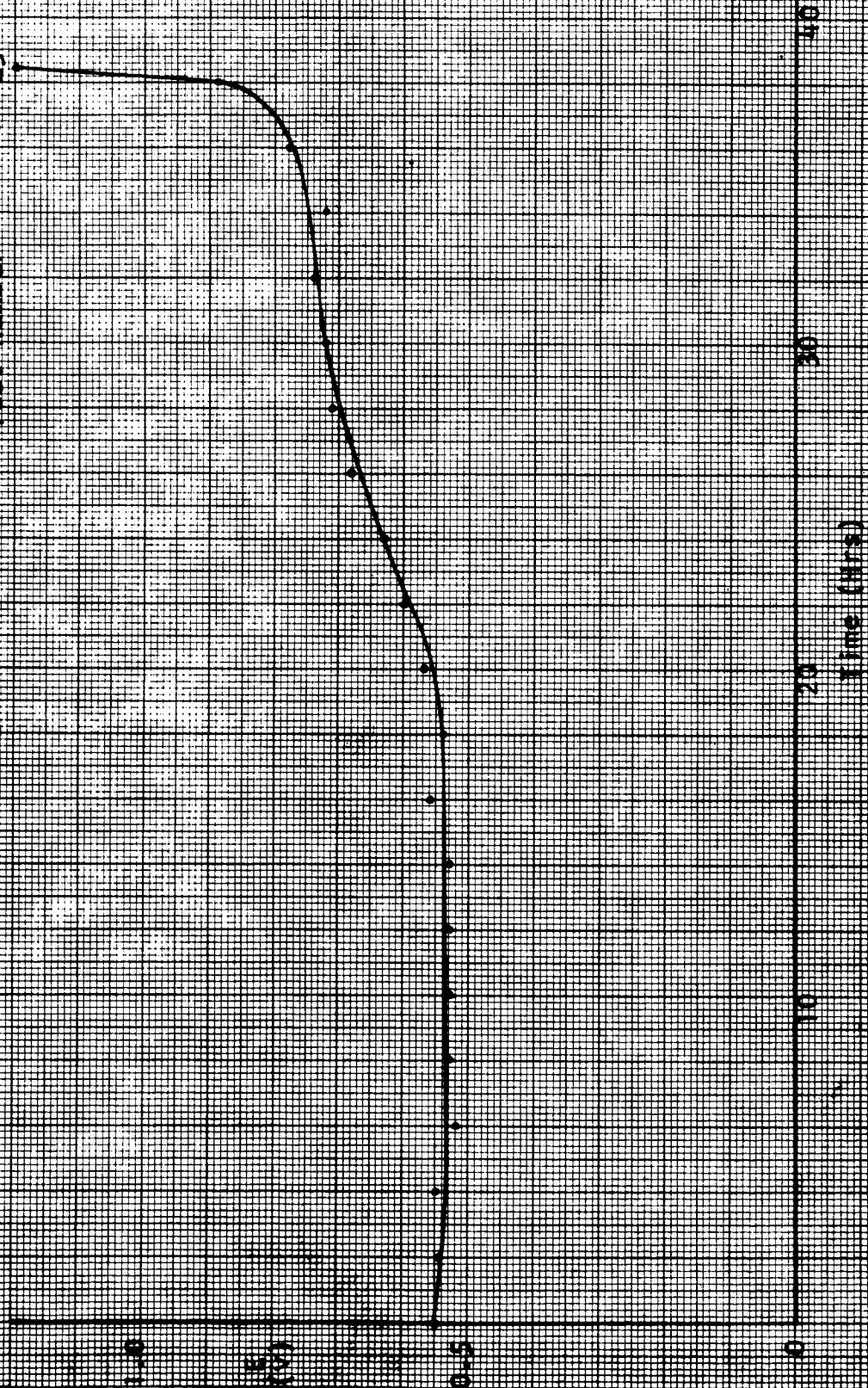


Figure 36

Ref. Electrode --- Ag/D.13M AgCl
Temp. --- $42.7 \pm 5^\circ\text{C}$; $i = 264 \text{ ma}$

E vs. t Data
2-day Test
Copper Needle Cathodes
25% CuO + 75% Cu₂O

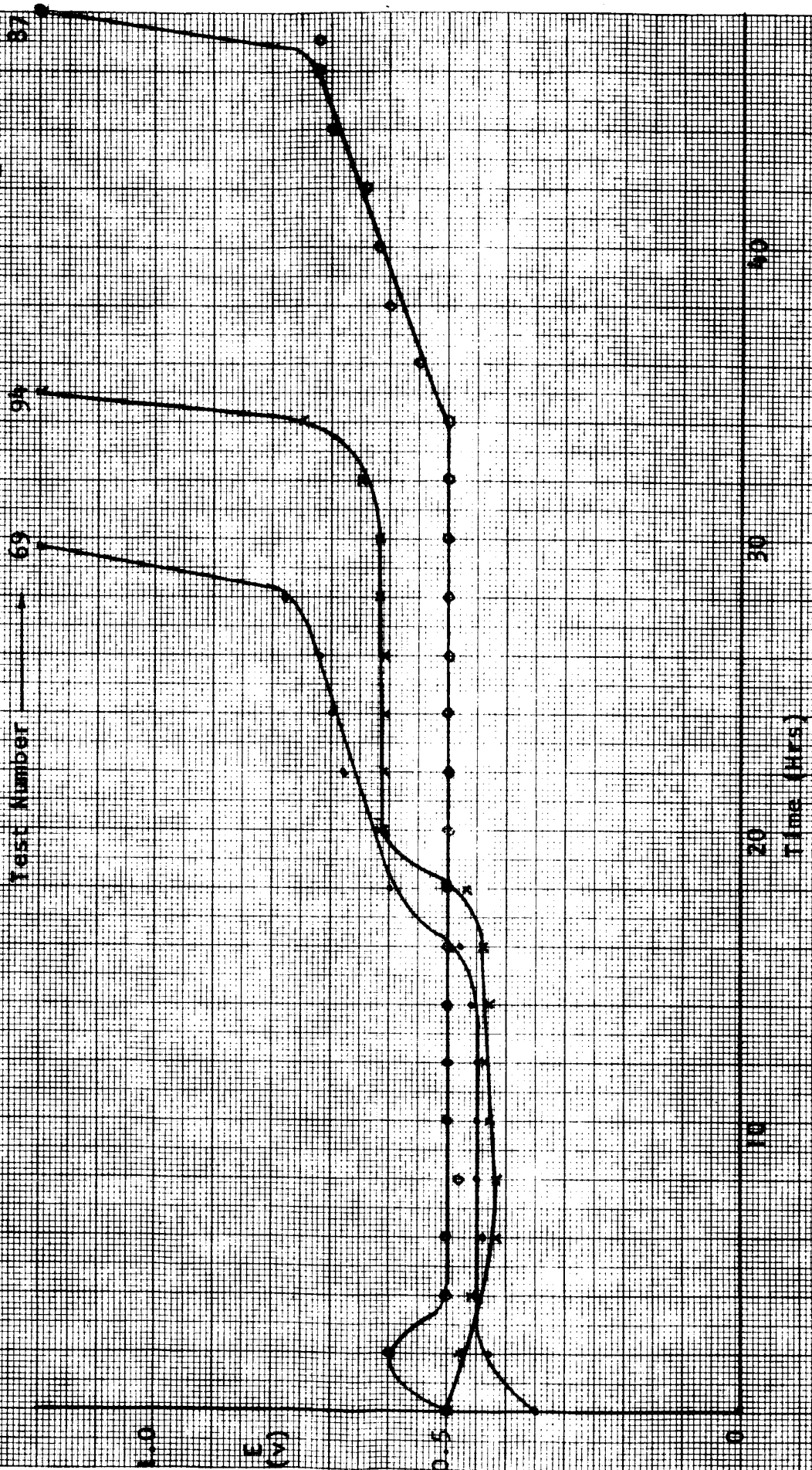


Figure 37

Ref. Electrode --- Ag/0.13M AgCl
 Temp. --- 427 ± 5°C | = 264 ma

E vs. t Data

2-Day Tests
 Copper Needle Cathodes
 100% Cu₂O

Test Number

60

80

93

10

20

30

40

Time (Hrs)

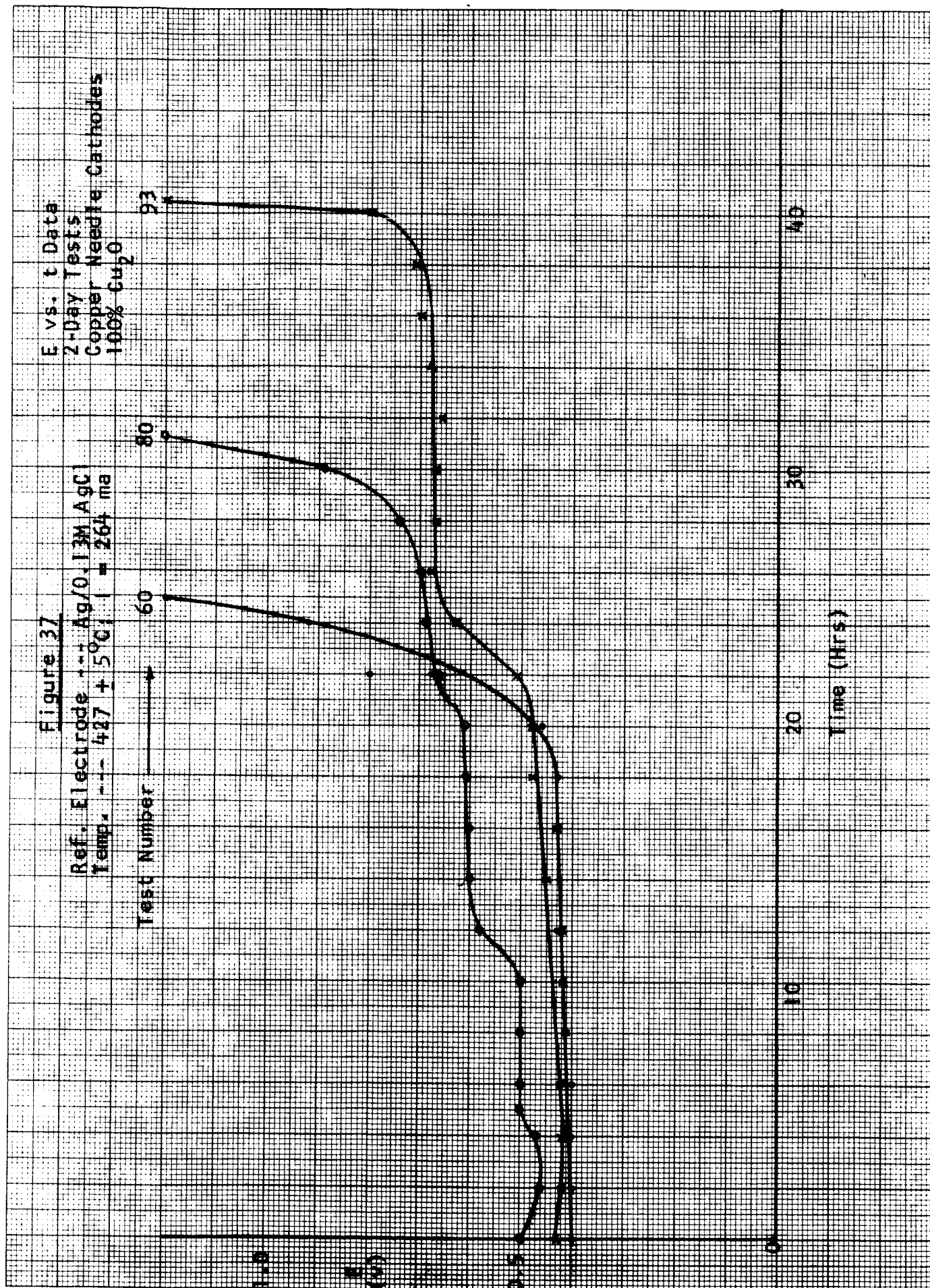


Figure 38

Ref. Electrode --- Ag/0.13M AgCl
Temp. --- 427 ± 5 C; t = 87.5 ms

E vs. t Data
6-Day Tests
Copper Needle Cathodes
100% CuO

Test Number → 70 95 71

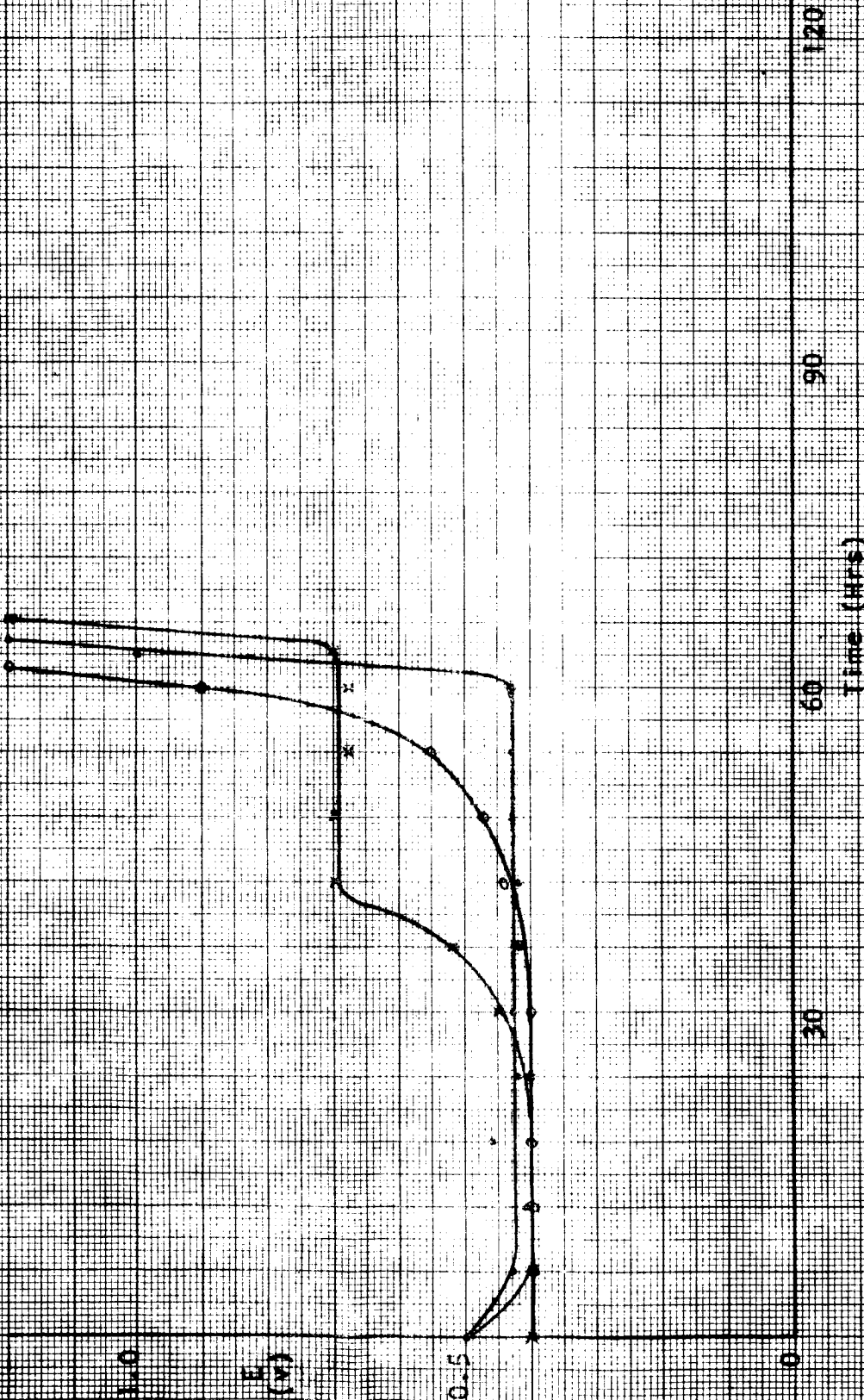


Figure 32

Ref. Electrode --- Ag/0.1M AgCl
Temp. --- 427 ± 5°C; I = 87.5 ma

E vs. t Data

6-Day Tests
Copper Needle Cathodes
25% CuO + 75% Cu₂O

Test Number → 109

54

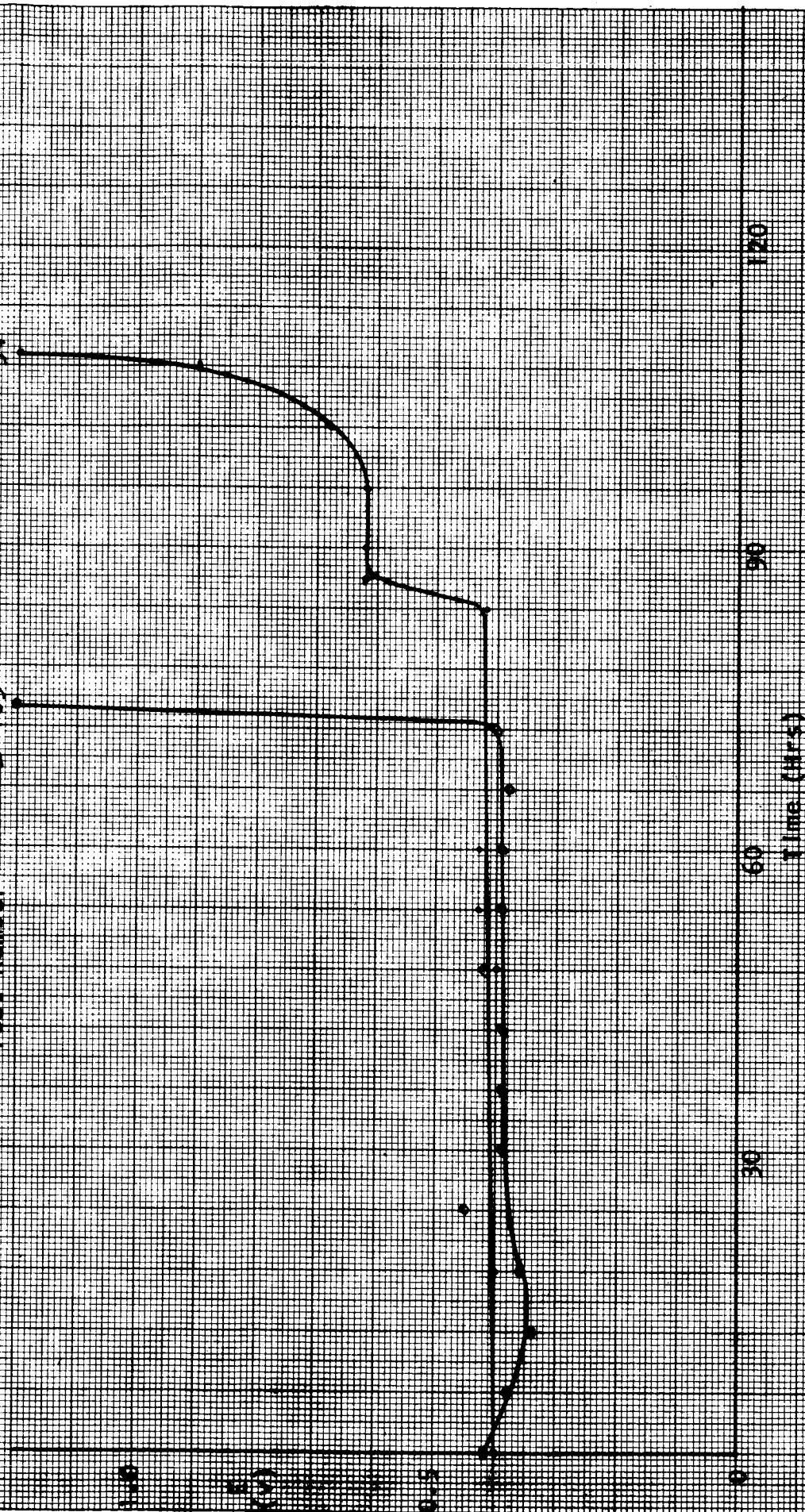


Figure 40

Ref. Electrode --- Ag/0.13M AgCl
Temp. --- 427 ± 5°C; I = 87.5 ma

E vs. t Data
6-Day Tests
Copper Needle Cathodes
100% Cu₂O

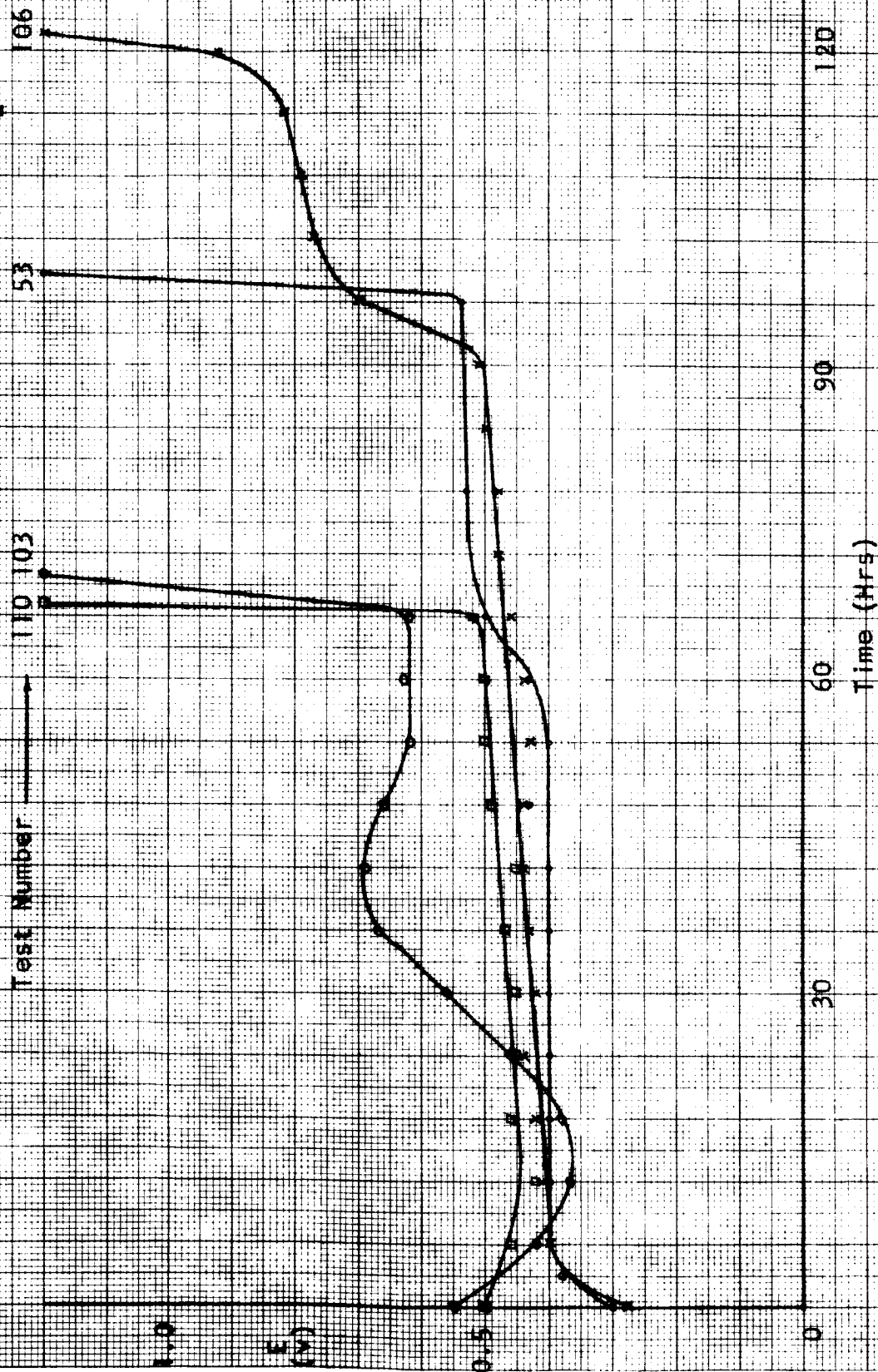


Figure 41

Ref. Electrode --- Ag/0.13M AgCl
Temp. --- 427 ± 5°C; I = 264 ma

E vs. t Data
2-Day Tests
Copper Grid Cathodes
100% CuO

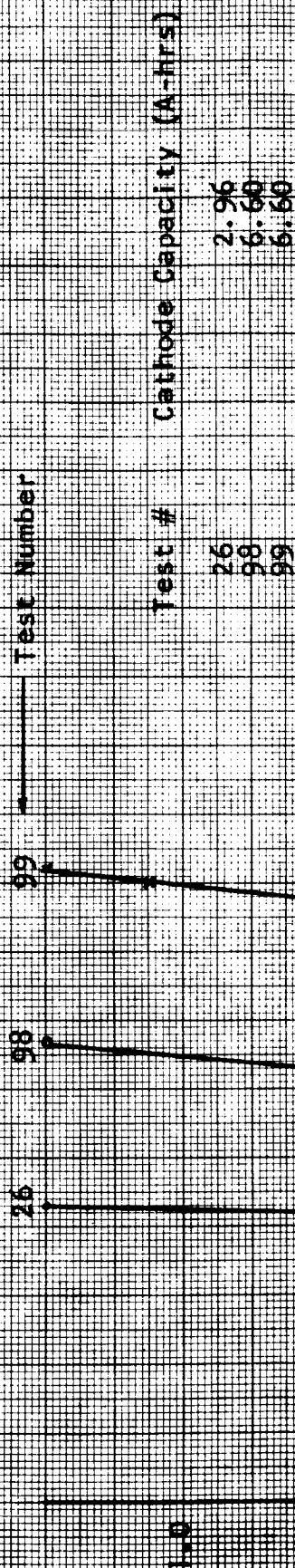


Figure 42

Ref. Electrode -- Ag/0.1M AgCl
 Temp. -- 27 ± 5°C | 264 Hz

E vs. t Data
 2-day Test
 Copper Grid Cathode
 50% CuO + 50% Cu₂O
 3.2 A-Nr/s

Test Number

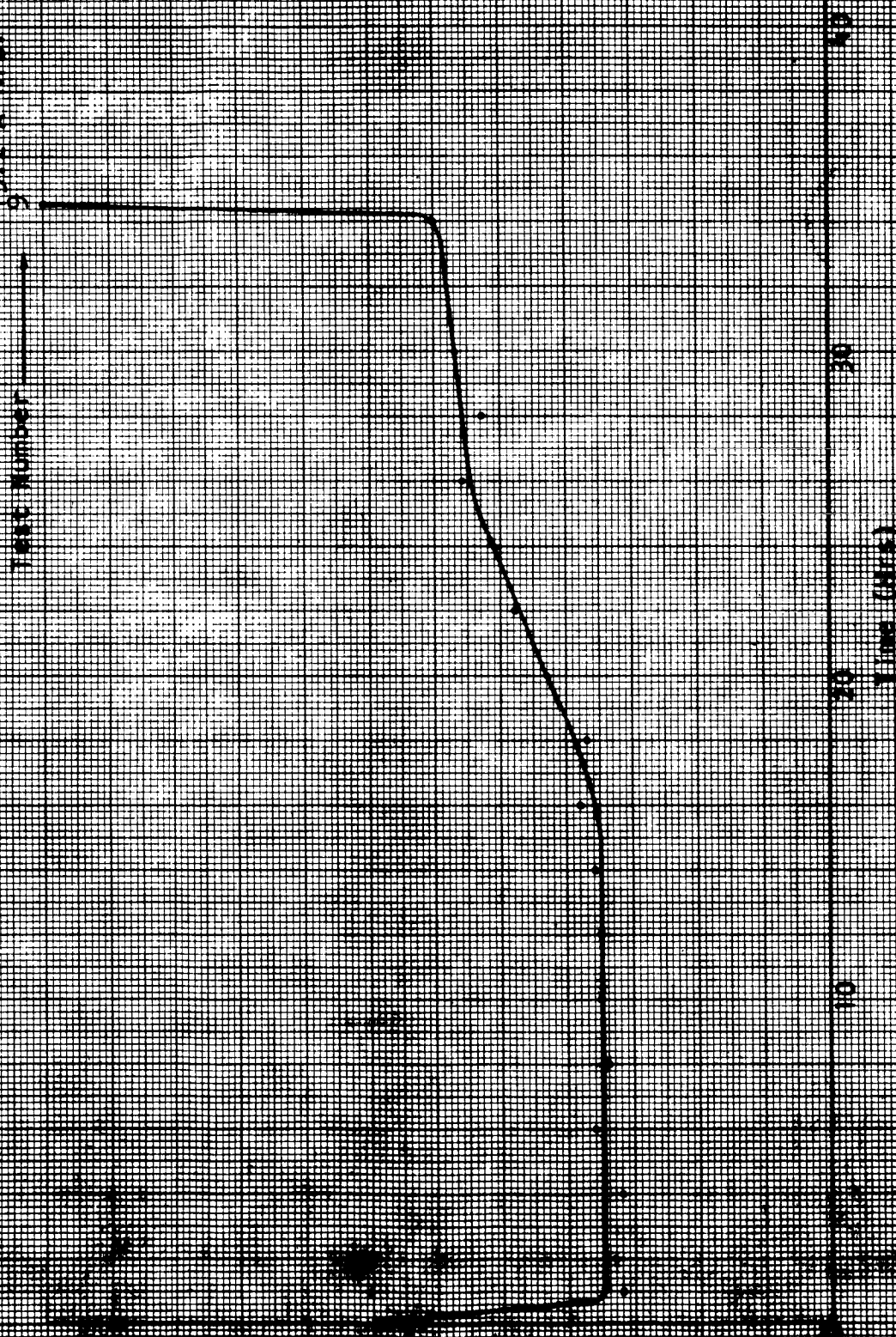


Figure 43

Ref. Electrode --- Ag/0.13M AgCl
Temp. --- 427 ± 5°C; $i = 264$ ma

Test Number --- 67

E vs. t Data
2-Day Test
Copper Grid Cathode
25% CuO + 75% Cu₂O
Cathode Capacity = 7.2 A-hrs



Figure 44

Ref. Electrode --- Ag/0.13M AgCl
Temp. --- 42.7 ± 5°C, I = 264 ma

E vs. t Data
2-Day Tests
Copper Grid Cathode
100% Cu₂O

Test Number → 81 88

Test # Cathode Capacity (A-hrs)

81 5.90
88 5.95

1.0
0.5
0
E (v)

0

10

20

30

40

Time (Hrs)

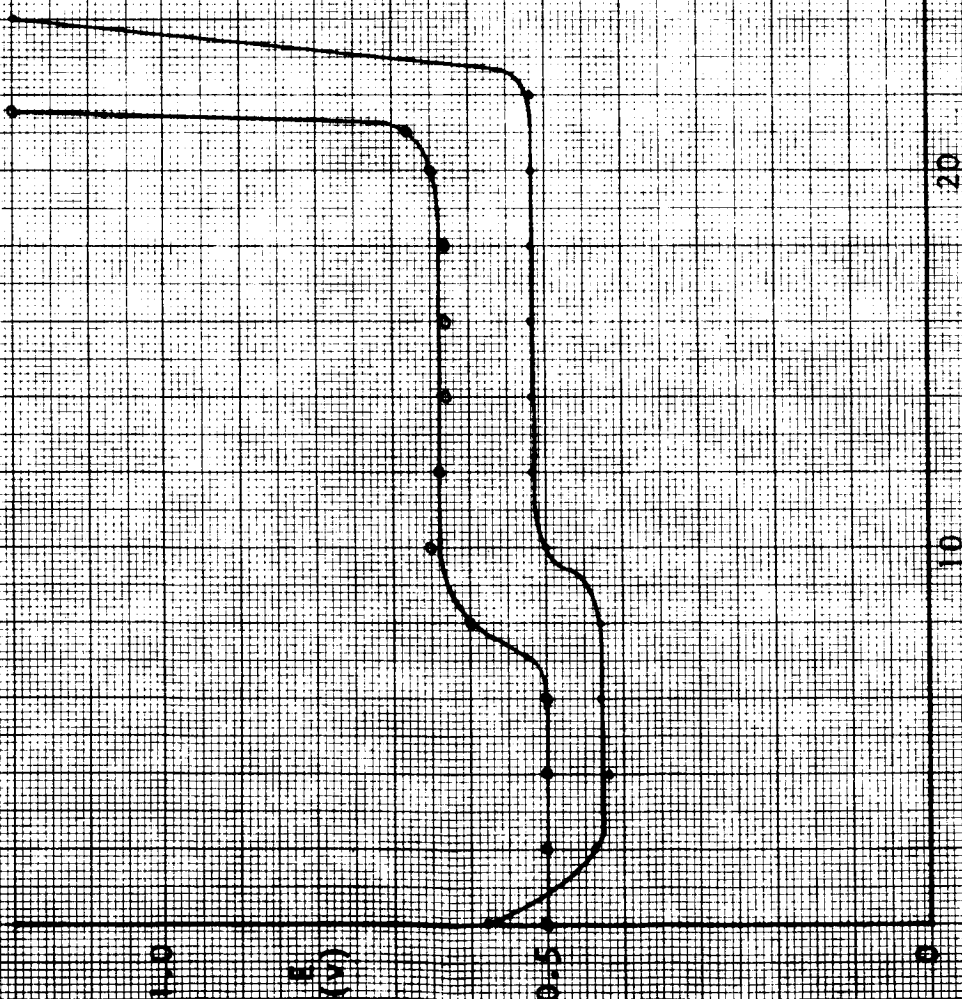


Figure 45

Ref. Electrode: $\text{Ag}/0.1\text{N AgCl}$
 Temp.: $27 \pm 5^\circ\text{C}$ $\pm 0.5\text{ mA}$

E vs. t Data
 6-Day Tests
 Copper Grid Cathodes
 100% CuO

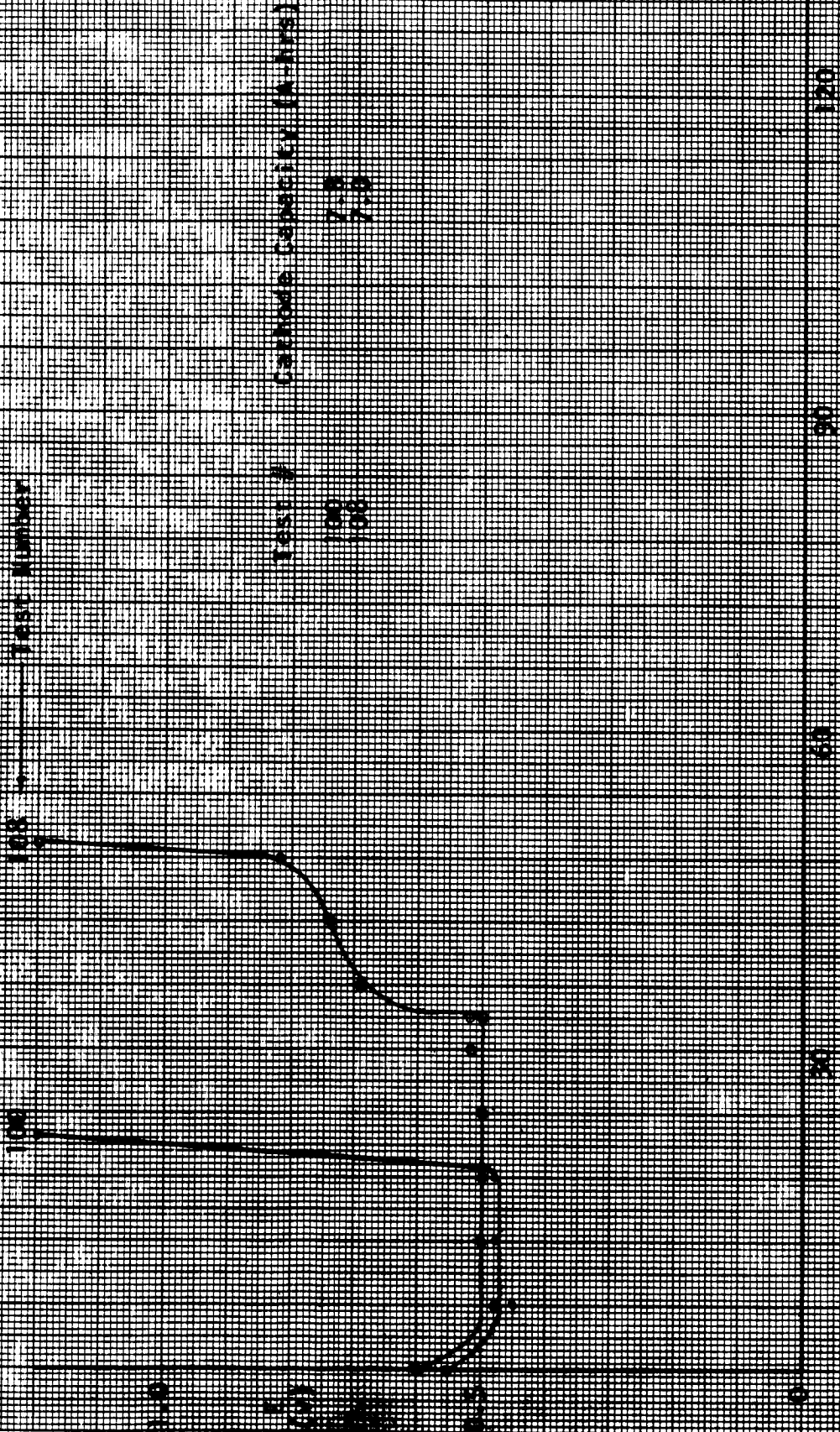
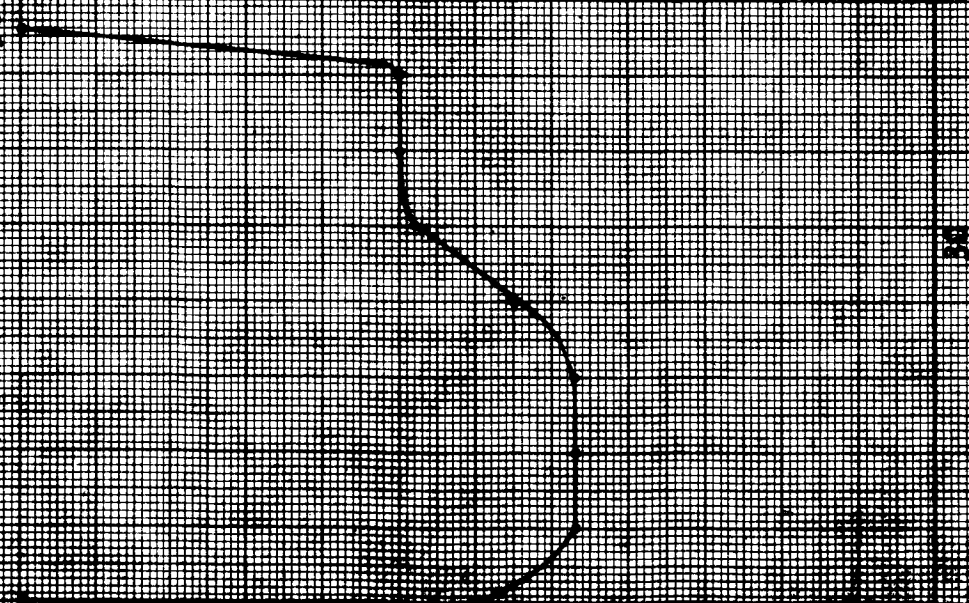


Figure 46

Ref. Electrode: Ag/AgCl (1M AgCl)
Temp.: $25 \pm 0.5^\circ\text{C}$ | $\sim 87.5 \text{ ms}$

Test Number: 56



E vs. t Data
6-Day Test
Copper Grid Cathode
25% CuO + 25% Cu_2O
6.5 A-hrs

Figure 47

Ref. Electrode -- Ag/0.1M AgCl
 Temp. -- $42.7 \pm 5^\circ\text{C}$; $i = 87.5 \text{ ma}$

E vs. t Data
 6-Day Test
 Copper Grid Cathodes
 100% Cu₂O

Test Number

105 107 68 55

Test # Cathode Capacity (A-hr)

55 5.3
 68 5.3
 105 5.3
 107 5.3

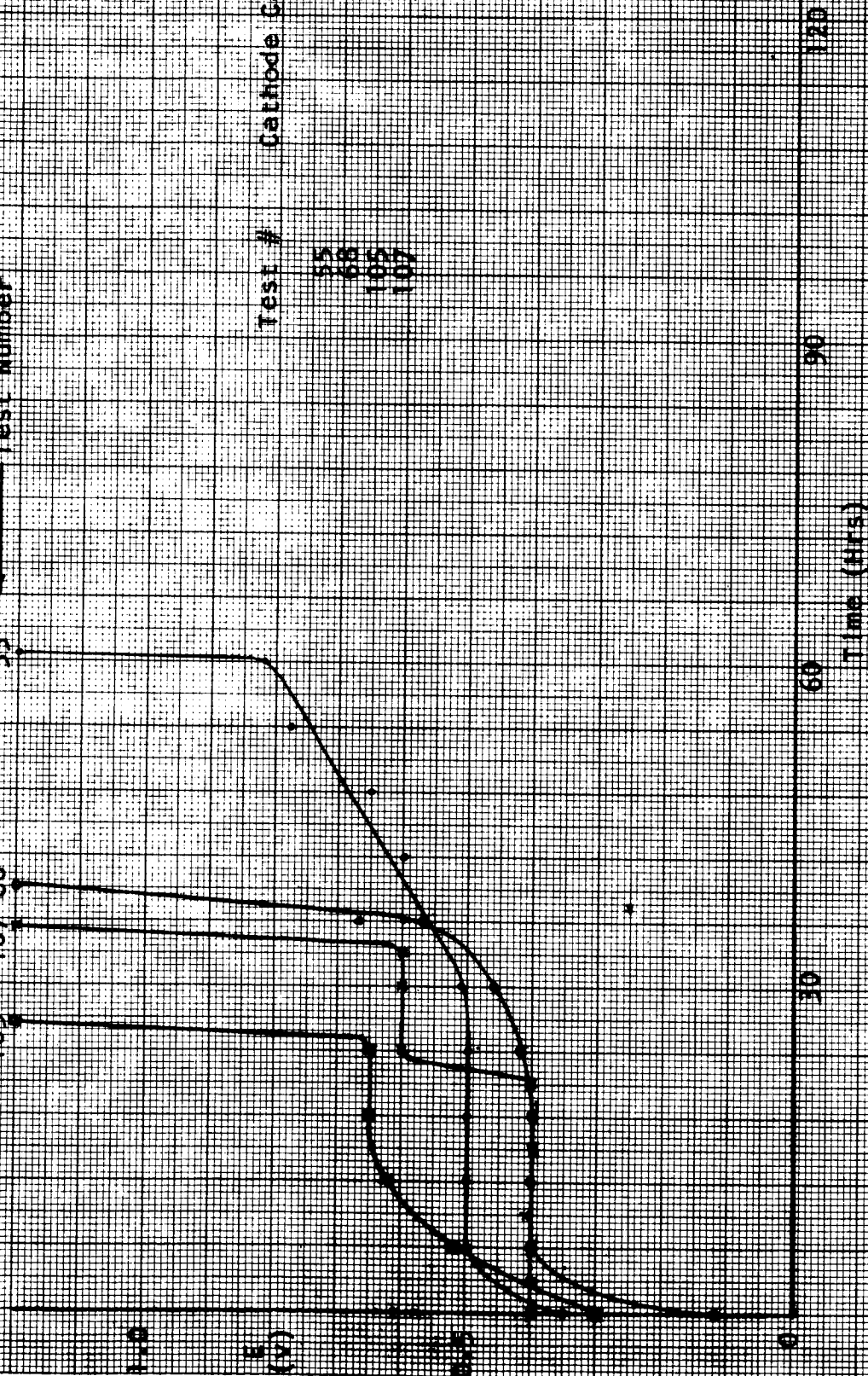


Figure 48

Ref. Electrode --- Ag/0.1M AgCl
Temp. --- 27 ± 5°C, 1 × 250 ms

Test Number --- 62

E vs. t Data
2-Day Test
Electrodeposited Copper
Cathode
100X (uV)
2.6 A-MF

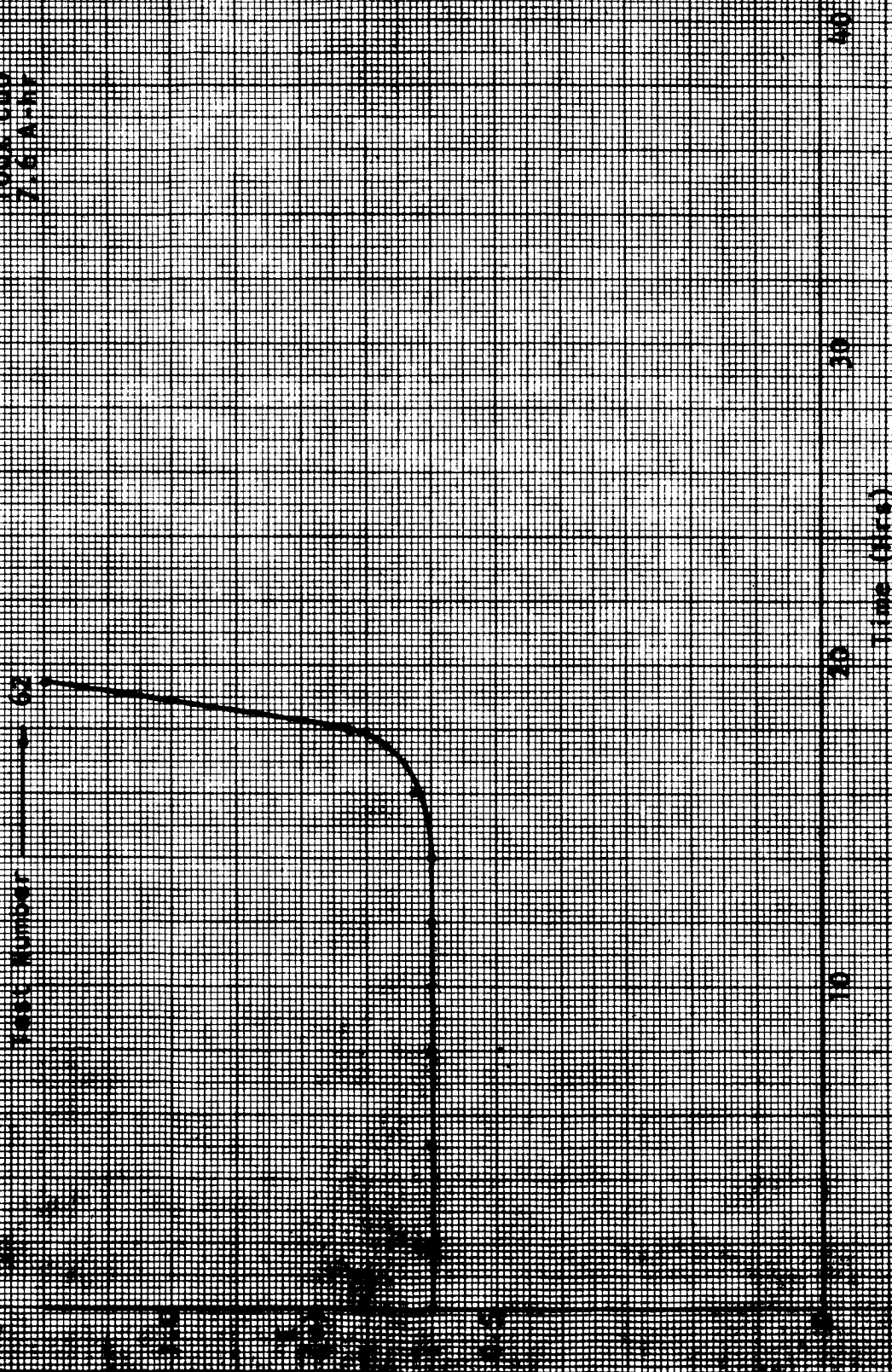


Figure 49

Ref. Electrode -- Ag/0.13M AgCl
Temp. -- $42.7 \pm 5.0^\circ\text{C}$ -- 264 ma

E vs. t Data

2-Day Test

Electrodeposit Copper

Cathode

25% CuO + 75% Cu₂O

4.7 A-hr

Test Number -- 63

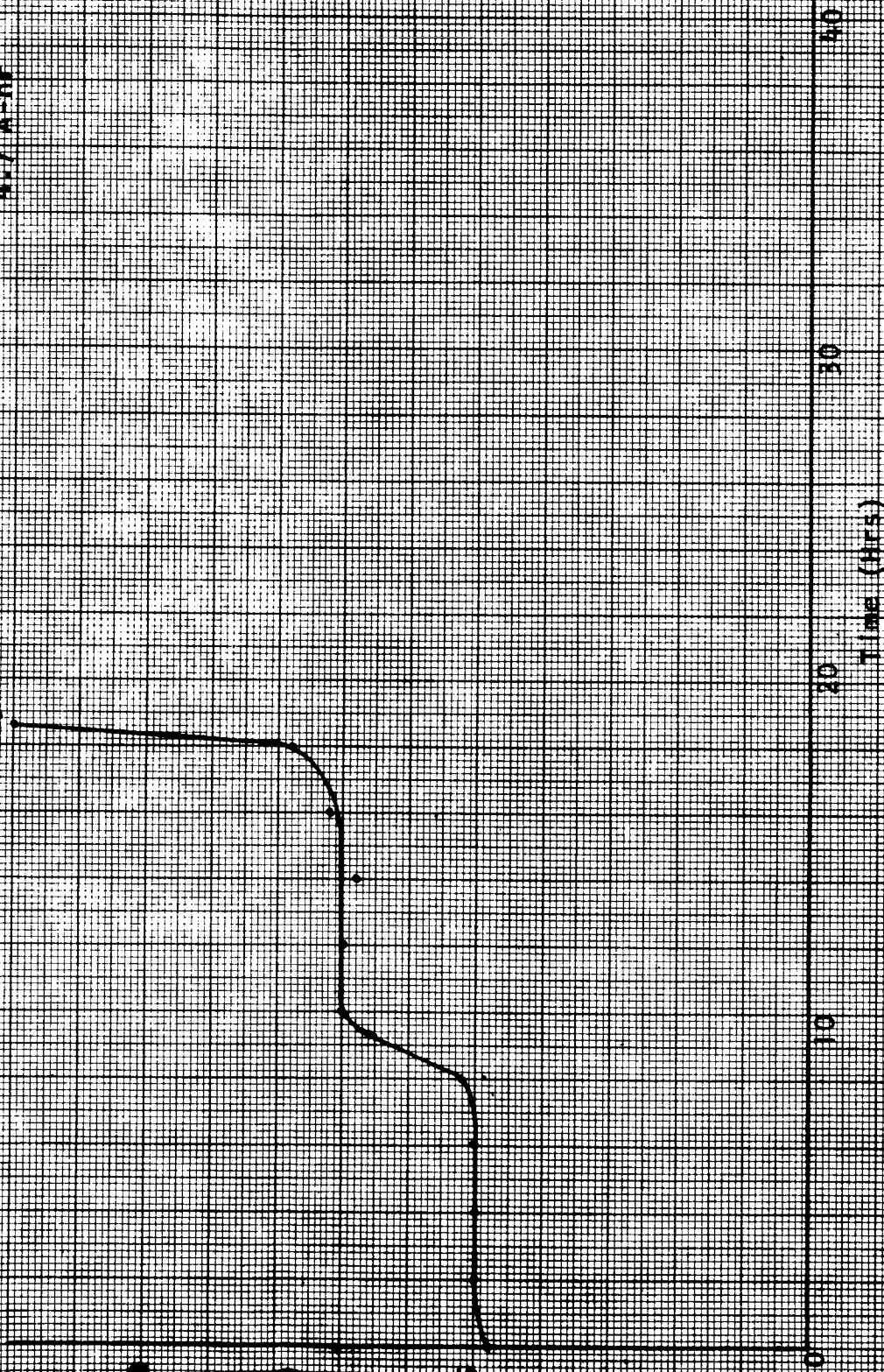


Figure 50

Ref. Electrode --- Ag/0.13N AgCl
Temp. --- 42.7 ± 5.0°C, I = 2.04 ma

Test Number → 66

E vs. t Data
2-Day Test
Electrodeposit Copper
Cathode
100% Cu₂O
0.3 A-hf.



Figure 51

Ref. Electrode --- Ag/0.13M AgCl
Temp. --- 427 ± 5°C; I = 87.5 ma

E vs. t Data
6-Day Test
Electrodeposit Copper
Cathode
100% Cu₂O
7.7 A-hr.

Test Number → 61

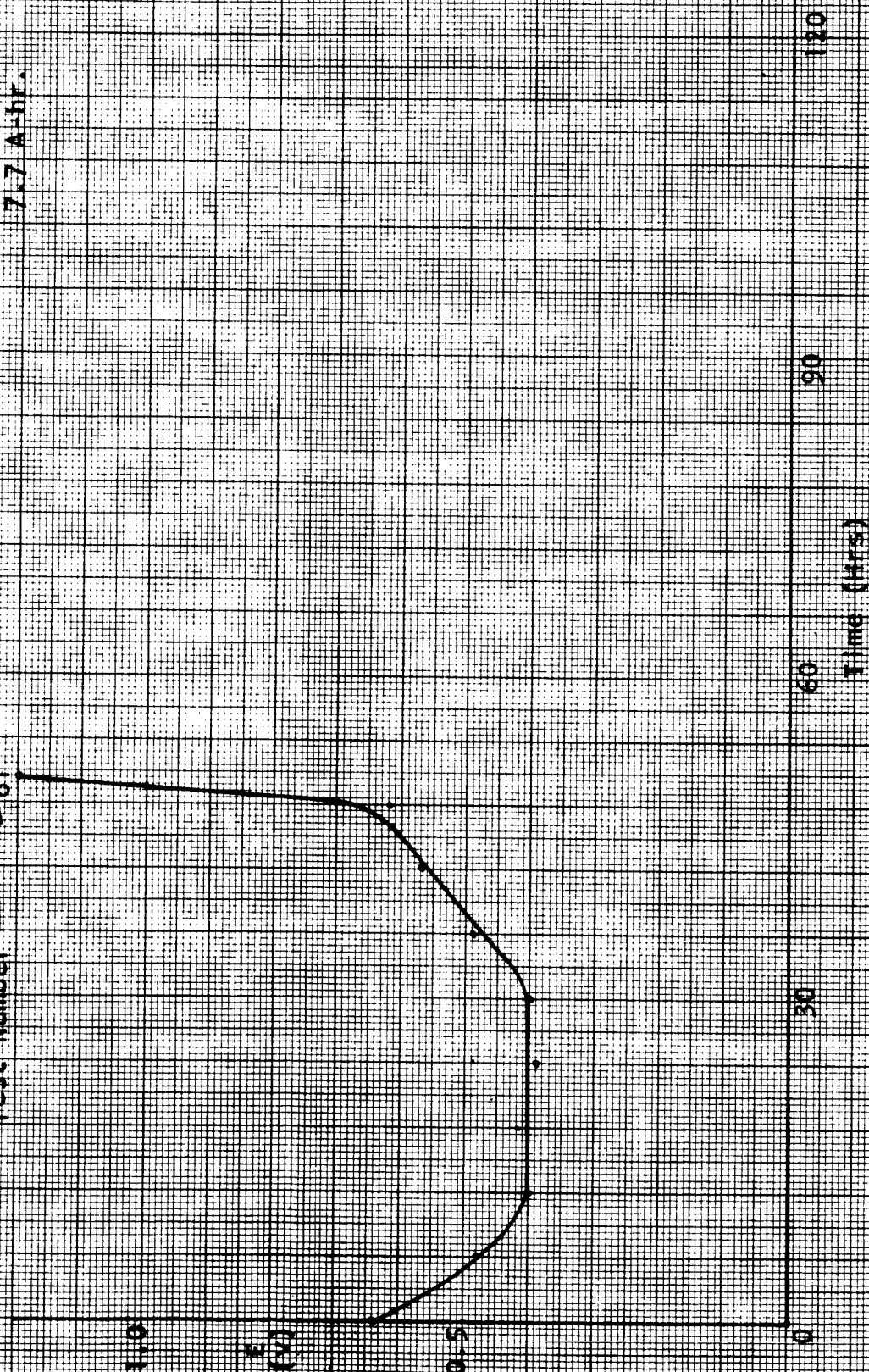


Figure 52

Ref. Electrode --- Ag/0.1M AgCl
Temp. --- 42.7 ± 50C

Test Number

60

30

60

90

120

Time (Hrs)

Electrode Data
6-Day Test
Electrodeposited Copper
Cathode
25% CuO + 75% Cu₂O
4.5 A-hr.

60

30

60

90

120

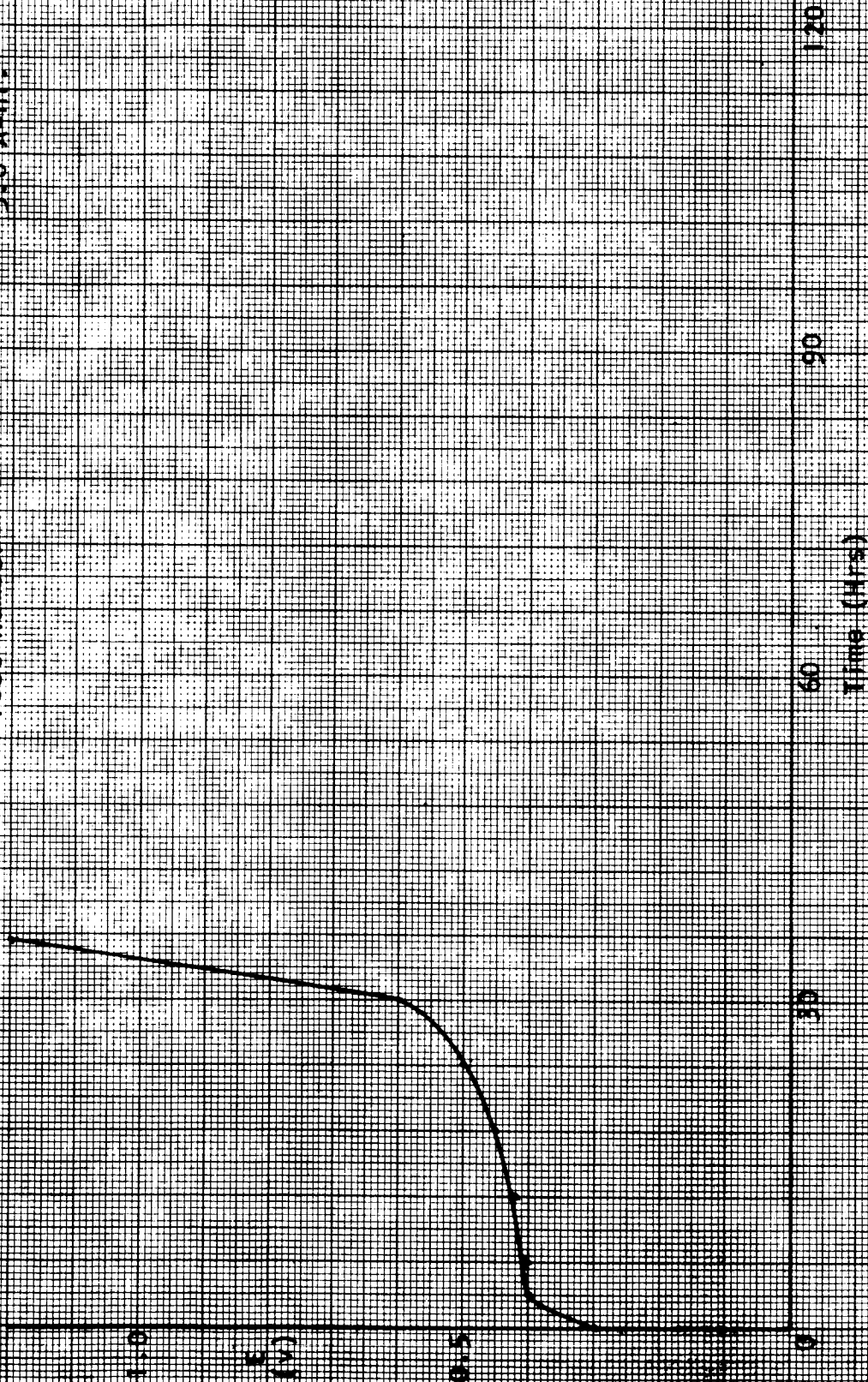
Time (Hrs)

Figure 53

Ref. Electrode --- Ag/0.13M AgCl
Temp. --- 42.7 ± 5.0°C; I = 87.5 ma

Test Number

65

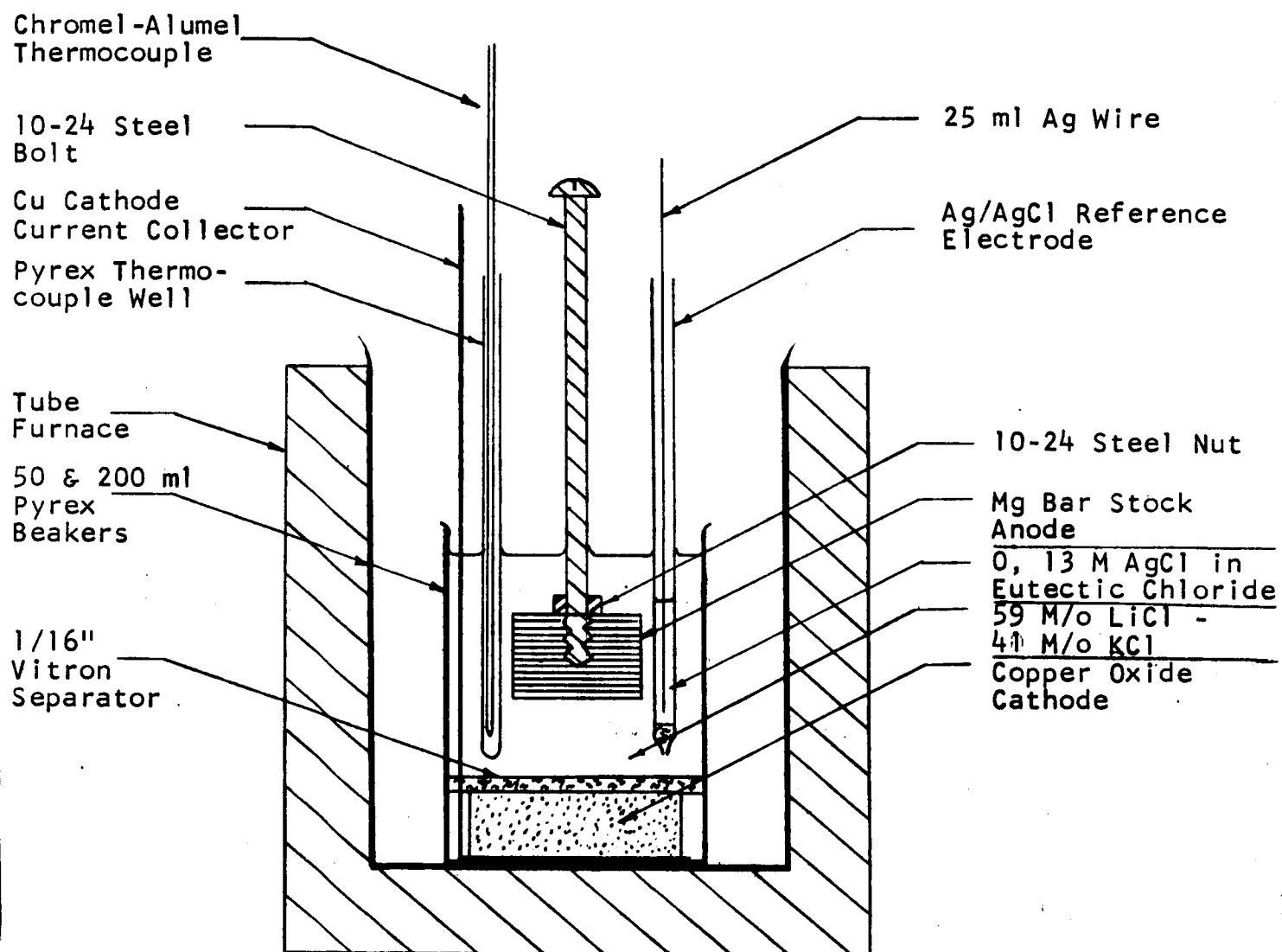


E vs. t Data
6-Day Test
Electrodeposit Copper
Cathode
100% Cu₂O
3.8 A-hr.

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Figure 54

Half-Cell Construction



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Figure 55

Measurement of the Resistance of LiCl/KCl
Over a 200 Hour Period

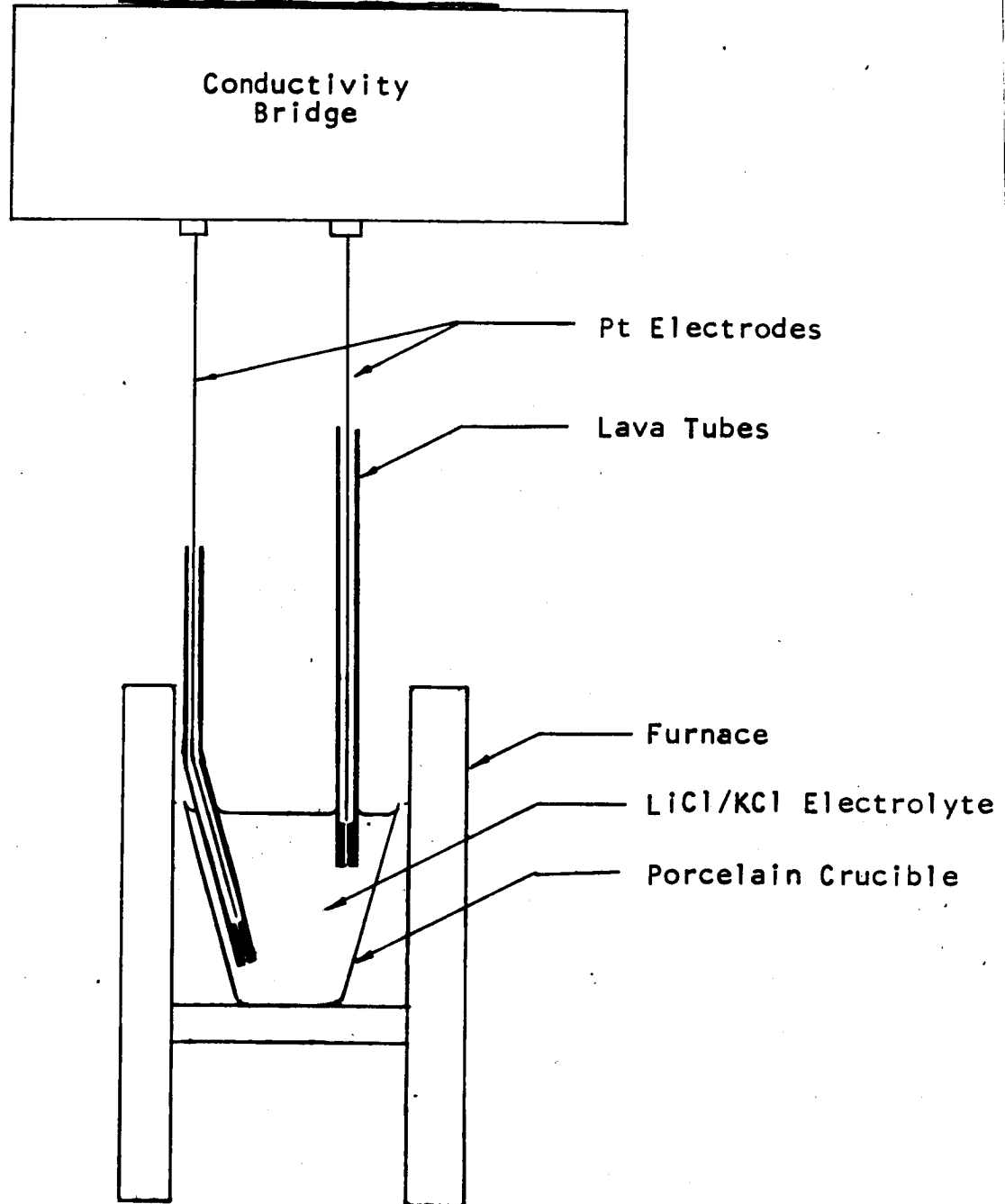


Figure 56

Separator Resistance Cell

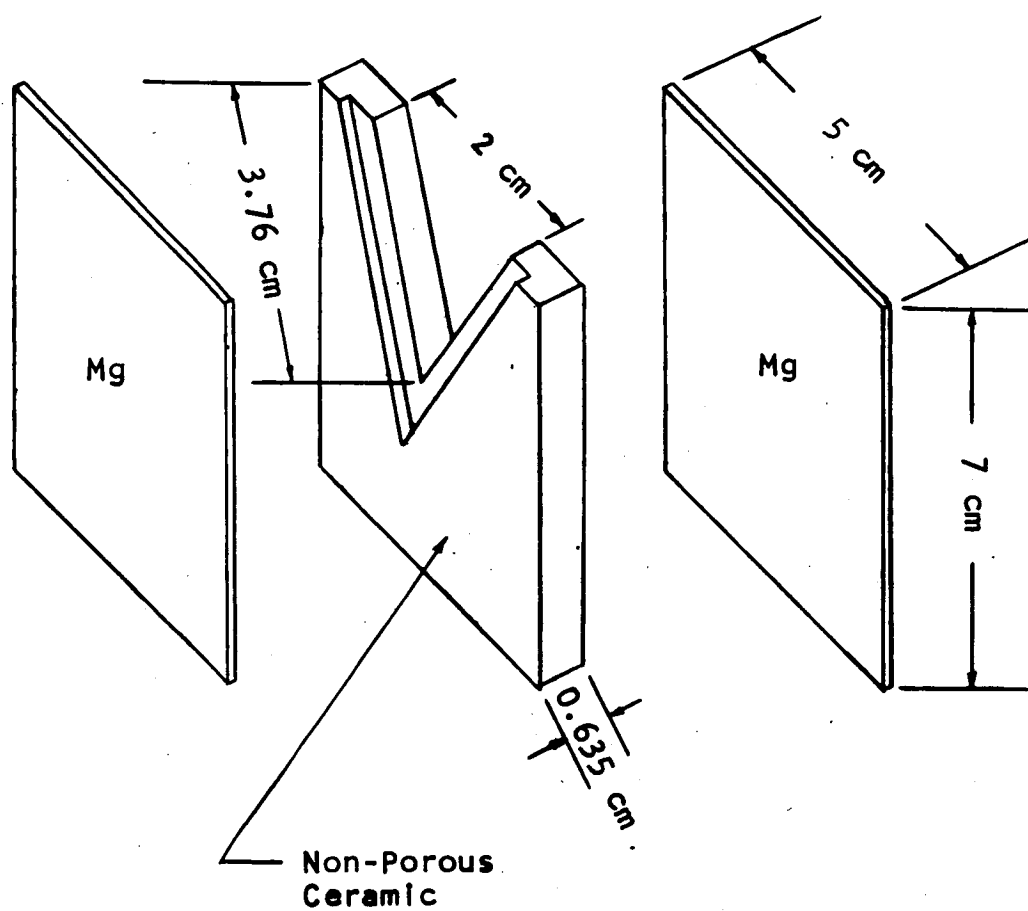
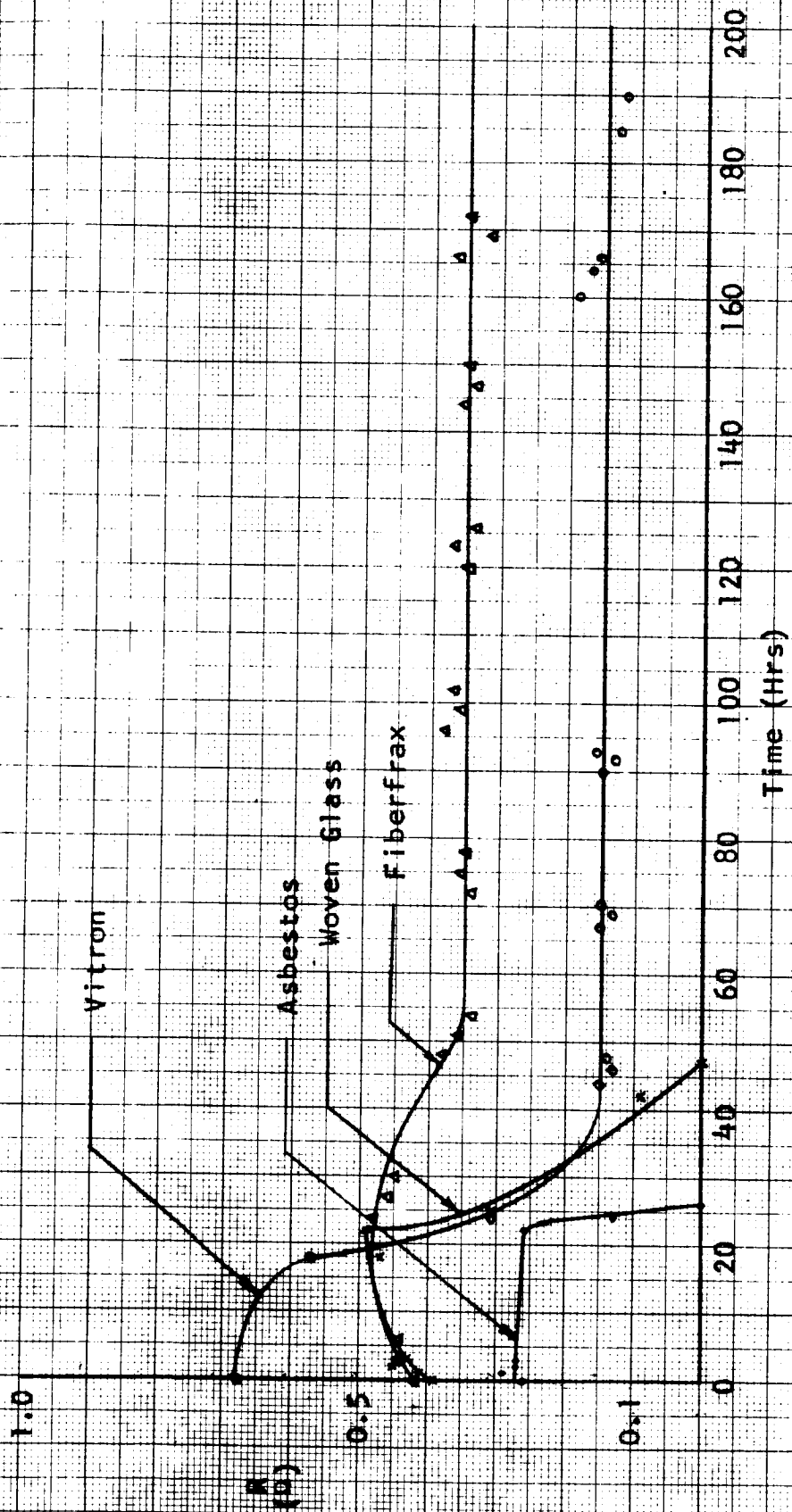


Figure 57

Separator Resistance vs. Time



APPENDIX II
ANALYSIS PROCEDURES

APPENDIX II

I. Preparation and Standardization of Ceric Sulfate Solution

A. Preparation of Ceric Sulfate Solution

1. Placed 500 ml. of distilled water in a 1500-ml beaker.
2. While constantly stirring the contents, 28 ml. of 36N H_2SO_4 was slowly added.
3. Weighed out 63 grams of $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$
4. Added this compound to the sulfuric acid solution and continuously stirred until the solid was dissolved.
5. The solution was diluted to approximately one liter and transferred to a clean, ground-glass-stoppered flask.
6. Ceric sulfate solutions are unaffected by light and thus a clear flask was used.

B. Standardization of Ceric Sulfate Solution Against Arsenious Oxide

1. Approximately one gram of As_2O_3 was dried at $100-105^\circ\text{C}$ for one hour.
2. Samples of 0.2 grams were accurately weighed out into each of three 500-ml flasks.
3. The As_2O_3 was dissolved in 10 ml of cold 6N NaOH. The mixture was swirled continuously until complete solution of the solid was obtained.

4. 75 ml. of water and 25 ml. of 6N H_2SO_4 was added.
5. Two drops of 0.01F OsO_4 reagent and 2 drops of 0.025F orthophenanthroline ferrous sulfate was then added.
6. These prepared solutions were titrated with the ceric sulfate solution until there was a pronounced local decrease in the pink color upon dropwise addition of the ceric sulfate solution. Thereafter the ceric sulfate was added in fractions of a drop until the pink color of the indicator was no longer perceptible.
7. An endpoint correction was obtained by similarly titrating a solution having the same volume as did the titrating solution, and prepared with the same amounts of NaOH, H_2SO_4 , OsO_4 and indicator. The end point correction normally was about 0.03 ml.
8. The end-point correction was subtracted from the standardizing titration and the normality of the ceric sulfate solution was calculated.

II. Preparation and Standardization of Thisulfate Solutions

A. Preparation of Thisulfate Solutions

1. One liter of distilled water was brought just to the boiling point and allowed to slowly boil for 5 minutes.

2. Twenty-five (25) grams of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and 0.1 gram of Na_2CO_3 was dissolved in the freshly boiled water after cooling.
3. The solution was transferred to a clean ground - glass-stoppered bottle.

B. Standardization of Thiosulfate Solutions

1. Samples of clean, dry copper foil was accurately weighed of such size to require from 25 to 35 ml of the thiosulfate solution.
2. The samples were transferred to 200-ml flasks.
3. Five milliliters of 6N HNO_3 were added, the flasks covered with a watch glass, and gently heated to dissolve the metal.
4. When the solution was complete, the watch glass was removed and 10 ml. of 18N H_2SO_4 was added.
5. The solution was evaporated on a hot plate until the H_2SO_4 gave off copious dense white fumes.
6. The solution was allowed to cool.
7. One milliliter portions of water was added until a total of 5 milliliters had accumulated after which 15 ml. additional was added.
8. The solution was boiled for 1-2 minutes and allowed to cool to room temperature.
9. While constantly swirling the cold H_2SO_4 solution, 15N NH_4OH was slowly added until the first perceptible blue color of the cupric ammine complex was obtained.

10. Six normal H_2SO_4 was added dropwise until this blue color just disappeared and then 1 ml. was added in excess.
11. The solution was again cooled to room temperature.
12. Four grams of KI was dissolved in 10 ml. of water and added to the copper containing solution.
13. The solution was swirled gently and continuously and immediately titrated with the thiosulfate solution. The thiosulfate was added rapidly until the color of the iodine became indistinct.
14. Three milliliters of starch indicator solution was added and titrated almost to the disappearance of the starch color.
15. Two grams of KSCN was added and titrated to the disappearance of the starch color.
16. The buret reading was recorded and the normality of the thiosulfate was calculated.

III. Electrolytic Determination of Copper

1. In a 200-ml beaker a solution was prepared containing ~0.2 grams of copper per 100 ml. This was done by dissolving the Cu_2O and CuO in 12N HCl .
2. Five milliliters of 6N HNO_3 was added and the solution was carefully evaporated to dryness.
3. One hundred milliliters of water was added after cooling the beaker.

4. Two milliliters of 36N H_2SO_4 and 1 ml of freshly boiled 16N HNO_3 was added to the solution.
5. The platinum electrodes were cleaned in hot 6N HNO_3 , rinsed thoroughly with water, dried in air and finally the cathode was weighed.
6. The electrodes were attached to the power source and the beaker was raised into position so that the electrodes reached nearly to the bottom but yet not completely immersing the electrodes.
7. A split watch glass was placed on the beaker top to prevent loss of solution from bubbling.
8. With the maximum resistance in the circuit, the current was initiated.
9. Using a glass propeller, a stirrer was placed in operation.
10. The current was adjusted to 3-4 amperes.
11. The solution was electrolyzed until the blue color in the solution disappeared.
12. Twenty-five milliliters of water was added to elevate the solution level on the cathode.
13. The solution was electrolyzed 15 minutes more at 1 amp.
14. If no copper appeared on the freshly immersed surface, the deposition was considered complete. Otherwise electrolyzing continued until this test showed no further deposition of copper.

15. When the electrolysis was complete, the beaker was slowly lowered while directing a stream of water over the electrode.
16. When the electrodes were completely free of the solution, the current was turned off.
17. The cathode was rinsed in methanol and allowed to dry at room temperature.
18. The cathode was weighed and the weight of copper deposited was calculated.
19. The percentage of copper as the oxide was calculated.

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Churchill Borough
Pittsburgh, Pennsylvania 15235
Attention: Dr. A. Langer

Whittaker Corporation
Controls & Guidance
9601 Canoga Avenue
Chatsworth, California 91311
Attention: Dr. M. Shaw

Yardney Electric Corporation
Yardney Building
40-52 Leonard Street
New York, New York 10013
Attention: Dr. George Dalin

Catalyst Research Corp.
6101 Falls Road
Baltimore, Md. 21209

J. R. Moser 7
R. L. Blucher 2
H. J. Goldsmith 1
D. Ciganovic 1